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ABSTRACT

This book provides a basic introduction for the student to hazardous materials chemistry. Coverage of chemistry, rather than non-chemical hazards, is particularly stressed on a level which the layman can understand. Basic terminology is emphasized at all levels, as are simple chemistry symbols, in order to provide the student with an introductory knowledge of the language of hazardous materials. Seventeen chapters cover: (1) an introduction to chemistry, atoms, elements, and the periodic table; (2) bonding in molecules and an introduction to inorganic chemistry; (3) an introduction to organic chemistry; (4) alkenes and alkynes; (5) alcohols; (6) ethers; (7) an introduction to the carbonyl functional group; (8) ketones and aldehydes; (9) carboxylic acids, esters, and amides; (10) nitriles and amines; (11) aromatic compounds; (12) flammable materials; (13) physical/chemical properties; (14) compressed gases; (15) corrosive materials; (16) two additional EPA hazard characteristics; and (17) toxicological properties. Department of Transportation definitions and classes of hazardous materials are appended. (LZ)

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Hazardous Materials Chemistry for the Non-Chemist

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A featured speaker at hazardous materials workshops through the U.S., Professor Enholm is also a member of the American Chemical Society.

Preface

This book provides a basic introduction for the student of several related disciplines and backgrounds to hazardous materials chemistry. The scope of the book is quite different from any other text. Coverage of chemistry, rather than non-chemical hazards, is particularly stressed on a level which the layman can understand. It is aimed at the person who needs a basic introduction to chemistry, focused at a very fundamental and understandable level. No prior knowledge is assumed in this book. It should appeal to those whose work is in the area of hazardous waste management, hazardous waste treatment, legal aspects of hazardous chemicals and materials, and the storage and transportation of hazardous chemicals. Other important fields which overlap with this material may include fire-fighting, emergency first responders, laboratory work, environmental sciences and many others.

The book covers a variety of broad, yet important topics in hazardous materials chemistry. Basic terminology is emphasized on all levels, as are simple chemical symbols which are pertinent to the important areas of chemistry insofar as hazardous properties are concerned. This provides the student with an introductory knowledge of the language of hazardous materials and provides avenues for the communication of ideas,

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Chapter 1. An Introduction to Chemistry—Atoms, Elements, and the Periodic Table.

1.1 Introduction and Terms

Chemistry is the study of matter. *Matter* is anything which has mass and occupies space. It is what we see around us and it is found in one of three common states; all chemical compounds, mixtures, solutions, and elements exist in one of these three forms:

solids--most elements are solids at room temperature
liquids--only five elements are liquids: mercury and bromine are the most common but gallium, cesium, and francium are also liquids at room temperature
gases--includes eleven non-metallic elements such as hydrogen, fluorine, chlorine, oxygen, and nitrogen.

At relatively low temperatures, matter is usually a solid. In this state, the molecules (or atoms) form regular crystalline-like patterns–much like a lattice-work. Although still in motion, the molecules oscillate in generally fixed positions. As the temperature increases, the fixed structure of the molecules disappears, and the matter "melts" into a liquid state. At still higher temperatures, the molecules move further apart, break free from the surface of the substance, and form a gas.

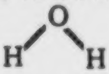
All matter consists of different types of atoms connected together to form innumerable substances. Atoms are incredibly small—100 million laid end-to-end would only be about one inch long! Yet these infinitesimal particles are what chemistry is all about. There are slightly more than 100 different types of atoms. Each type is called an element. There are 90 elements which occur naturally and 16 which have been synthesized. (i.e. prepared in a laboratory) All substances in our known universe are made from these known elements. As Paul W. Atkins, an *Oxford* Chemistry professor, stated in his masterful work, *Molecules:* "Let us marvel that so rich a tapestry can be woven from so meager a thread."

A pure substance is made of a single type of chemical and is typically found in only one physical state. It can be an individual *element* or a *compound.*

Examples:

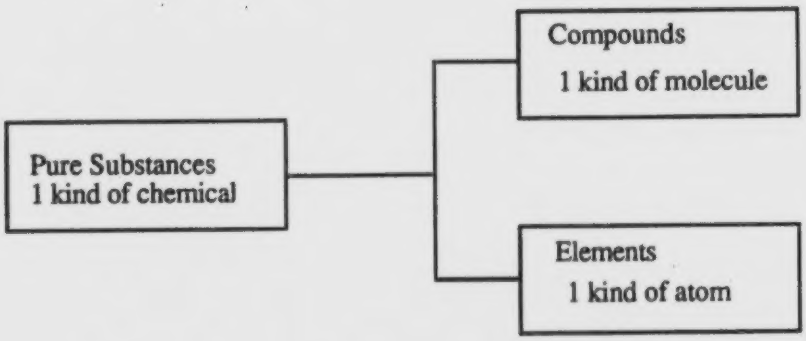
Zinc; = Zn (an element)
Sodium chloride = NaCl (a compound)

A *compound* is a pure substance made of one or more elements. These are not elements which are just mixed together. An actual chemical reaction takes place and bonds form between the atoms of the elements involved.

Example: H_2O =  (water) not just a mixture of oxygen and hydrogen (both are gases).

A *mixture* is a sample of matter which is made of two or more pure substances. When the substances are unreactive and similar in chemical behavior, they are compatible. This compatiblity factor is critical in determining what chemicals can be stored together in an unreactive state (sometimes for many years).

Examples: salt/water = $H_2O + NaCl$ (compatible)
sulfuric acid/sugar = $H_2SO_4 + C_{12}H_{22}O_{11}$ (incompatible)



Mass is a measure of the quantity of matter. A similar term is *weight*, which measures gravitational attraction.

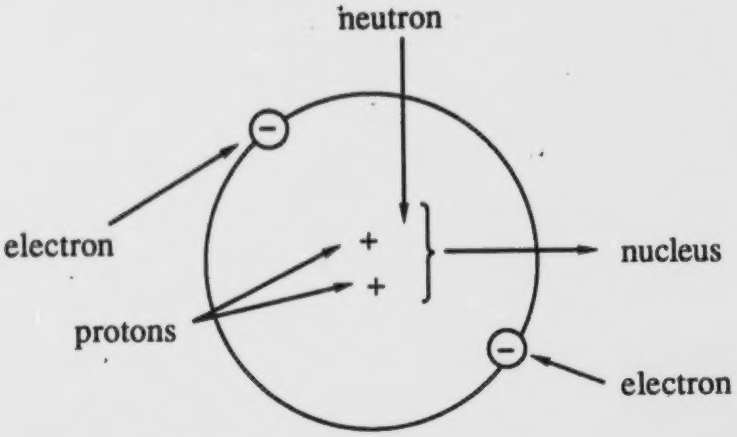
Example: A kilogram is a measure of mass equal to 1,000 grams.

Density is a measurement of mass per unit volume. It approximately measures the "heaviness" of a substance, such as the differences between a block of iron and a block of aluminum. Density is often expressed as grams per cubic centimeter or pounds per gallon.

$$\boxed{\text{Density} = \frac{\text{mass}}{\text{volume}}}$$

1.2 Atomic Structure

A Greek philosopher named Democritus hypothesized the existence of atoms in about 450 B.C. He proposed that if a material such as copper were subdivided enough times eventually what would be left is a particle of copper so small it could no longer be divided. He called this particle *atomos*, which means, literally, indivisible. It was an English scientist, John Dalton, in 1802 who first suggested that all matter could be broken down into elements, the smallest particles of which he referred to as "atoms".



By 1895, there was theoretical evidence for the existence of subatomic particles but it wasn't until 1913 that Niels Bohr developed the modern atomic theory He pictured an atom as consisting of three basic types of particles: **electrons, protons,** and **neutrons**. An electron is a particle having a negative one charge (-1). A proton is a particle with a positive one charge (+). A neutron is a particle with no electrical charge. The proton and neutron have essentially the same weight— one atomic mass unit (amu). An electron, by contrast, is only about 1/2000th this size! From a chemical point of view we can consider the mass of an electron to be zero. In the Bohr model, protons and neutrons are packed together in the center of the atom called the nucleus. Electrons travel around the nucleus in energy shells at relatively long distances from the nucleus. If fact, the average nucleus occupies only one ten-thousandth of the total volume of the atom. All atoms exhibit three important characteristics summarized in Table 1.

1. All the different types of atoms have an equal number of protons and electrons and are therefore electrically neutral;

2. Since each element is different, its atomic structure must be different. Each element has an **atomic number**. This number represents the number of protons (and electrons) the element possesses. For example, every atom of hydrogen (atomic number 1) has one electron spinning around a single proton; each atom of mercury (atomic number 80) has 80 electrons spinning around the nucleus which contains 80 protons and several neutrons;

3. An equal number of atoms of different elements weighed under the same conditions have a different weight. This weight is the sum of the number of protons and neutrons in the nucleus of the atom and is known as the **atomic weight** of the element. However each element has atoms which have a different number of neutrons in the nucleus. The atomic number is constant but the atomic weight is variable. These variations in atomic weight are referred to as **isotopes** of the element. There are over 2,000 known isotopes some of which are radioactive.

A final important characteristic of atoms is that the electrons revolve around the nucleus in a definite pattern. Groups of electrons maintain a specific average distance from the nucleus forming what are called energy shells. Each energy shell is capable of containing a finite number of electrons, the number increasing as the distance from the nucleus increases. There are seven known energy shells designated by letters—**k, l, m, n, o, p, q**—starting with the shell nearest the nucleus. The k shell can hold 2 electrons; the l & m shells 8 electrons; the n & o shells 18 electrons; and the p & q shells 32 electrons. The sequence is 2, 8, 8, 18, 18, 32, 32 for a total of 118 electrons. Scientists have only identified up to atomic number 107 (Unnilseptium). The outermost shell of an atom never contains more than eight electrons.

Characteristic	**Atomic Description**
Neutral atoms	Number of electrons = number of protons
Atomic number	# of protons = # of electrons = atomic number
Atomic weight	# of protons + # of neutrons = atomic weight

Table 1. Some Characteristics of Atoms

The following facts are true about atoms, which are similar to a tiny planetary solar system:

- Every atom has a dense and small nucleus
- The nucleus accounts for all of the positive charge and nearly all of the mass of the atom. (the electron has a very tiny mass)
- The nucleus is surrounded by a lot of empty space, which makes up the rest of the atom.
- The electrons which occupy the space around the nucleus have negative charges and balance (cancel) the positive charge in the nucleus.

1.3 The Periodic Table of the Elements

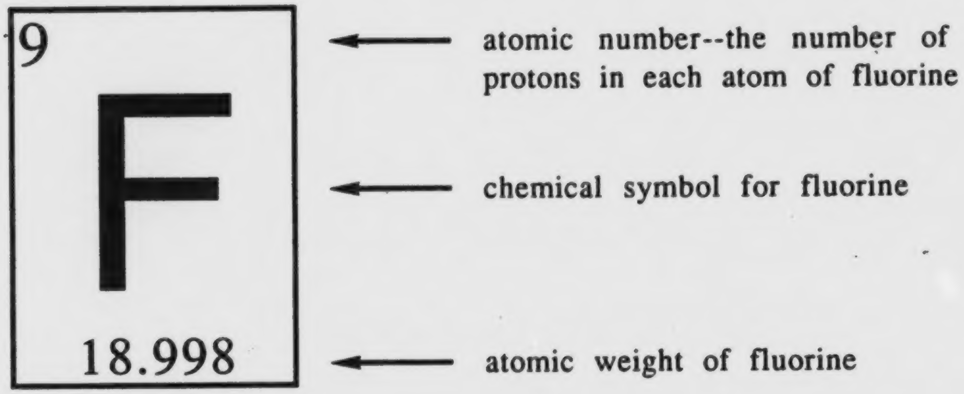
One of the most important advances in modern day chemistry was the development of the Periodic Table of the Elements. A closer look at this remarkable tool will enable even the neophyte to better understand the properties of elements and compounds.

The horizontal rows on the table are called *periods*, which vary substantially in length. The first period contains 2 elements, and the second and third have 8 elements each. The vertical columns are called *groups* or *chemical families*. These elements have similar physical and chemical properties. (Note especially column VII A, The Halogens, and column VIII A, The Nobel Gases.) The horizontal rows or *periods* of the table identify the seven different energy levels corresponding to the shells discussed earlier. The atoms in the center of the table are the B-row elements called "transition metals." Most other elements are in the A-row and are called "main group atoms." Note that elements 58—71 (the Lanthanide series) are atoms whose electrons fill suborbits within the p-shell differently than elements 72—86. Similarly, the Actinide series, elements 90—103 contain atoms whose electrons fill suborbits within the q-shell differently than elements 89—107.

1.4 Symbols for the Elements

You are no doubt familiar with many of the symbols for the elements. Chemists often use a single capitol letter to abbreviate the name of the element. Thus **N** is the symbol for nitrogen. When two elements begin with the same letter, a second lower-case letter is added. Thus **Ne** is the symbol for neon. The symbols for the eleven elements known in antiquity are taken from their Latin names: Copper *(Cuprum)* Cu; Gold *(Aurum)* Au; Iron *(Ferrum)* Fe; Lead *(Plumbum)* Pb; Mercury *(Hydrargyrum)* Hg; Potassium *(Kalium)* K; Sodium *(Natrium)* Na; Tin *(Stannum)* Sn; Antimony *(Stibum)* Sb; Silver *(Argentum)* Ag; Tungsten *(Wolfram)*. A chemical symbol is a more succinct way of referring to an element.

How to read an element on the table:


9
F
18.998
atomic number--the number of protons in each atom of fluorine
chemical symbol for fluorine
atomic weight of fluorine

Notice that the periodic table has all of the elements arranged by increasing atomic number. The chemical symbols have one or two letters, with the first always capitalized. There are over 103 different elements, however, only about 50 are ordinarily encountered in hazardous materials. About half of these are very commonly found in chemical compounds.

1.5 Periodic Law

In 1869, a Russian scientist and college professor, Dimitri Mendeleyev, using cards representing the 63 known elements, developed the first Periodic Table. Although other chemists had proposed systematic arrangements of elements before this, it was Mendeleyev's genius that enabled him to see that his table was incomplete. He left gaps and predicted the properties of the missing elements. These were subsequently discovered and found to be as he had predicted verifying his discovery of an important fundamental property of matter.

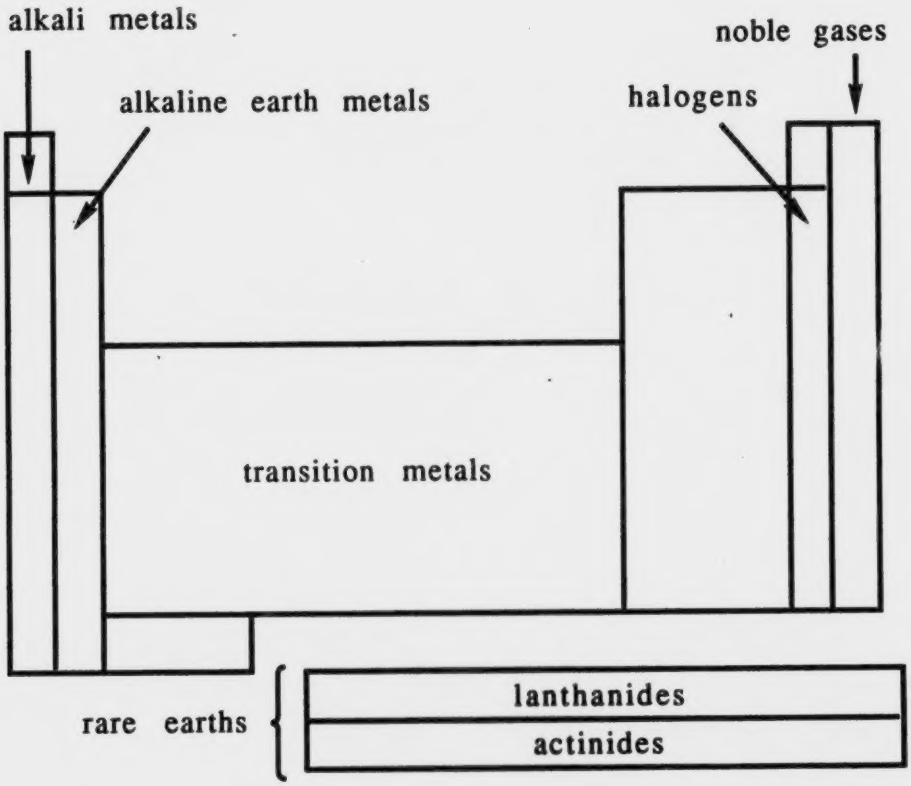
Today we know that electrons are the key to arrangement of elements on the Periodic Table. As each energy shell is filled, periodically the outermost energy shell contains the same number of electrons as a previous energy shell resulting in an element with similar physical and chemical properties. For example, consider lithium (Li) atomic number 3, sodium (Na) atomic number 11, and potassium (K) atomic number 19. The electron configuration of each lithium atom is 2, 1. The electron configuration of each sodium atom is 2, 8, 1; the electron configuration of each potassium atom is 2, 8, 8, 1. These elements all belong to a family called the Alkali metals. They exhibit similar properties because of their similar atomic structure.

Chemical reactions involve only the electrons in the outermost energy shell of an element. A chemical reaction has occurred only when the atoms of different elements have been rearranged. For example, sodium in column I A, has only one electron in the third energy shell; chlorine in column VII A, has seven electrons in the third energy shell (m—which can hold 8 electrons). These two elements combine together to form a compound—NaCl, common table salt. An important atomic property is that no element ever has more than eight electrons in its outermost energy shell.

1.6 Metals, Nonmetals, and Metalloids

Each element is classified as either a metal, nonmetal, or metalloid. A more recognizable term for metalloid is semiconductor. *Metals* are elements which conduct heat and electricity well, generally melt and boil at very high temperatures, possess relatively high densities, are normally malleable (able to be hammered into sheets) and ductile (can be drawn into a wire), and display a brilliant luster. Examples include zinc, mercury, nickel, platinum, and gold. All the elements to the left of the solid black line on the Periodic Table are metals.

The elements to the right of the solid black line are nonmetals. These elements generally melt and boil at relatively low temperatures, do not possess a luster, are less dense than metals, and hardly conduct heat or electricity, if at all. At room temperature bromine is the only liquid nonmetal. Helium, neon, argon, krypton, xenon, radon, oxygen, nitrogen, flourine, and chlorine are gases . The remaining nonmetals are solids at room temperature.


alkali metals
alkaline earth metals
halogens
noble gases
transition metals
rare earths
lanthanides
actinides

Six elements have properties resembling both metals and nonmetals. They are called metalloids or *semiconductors*. These elements are boron, silicon, germanium, arsenic, tellurium, and polonium. Although silicon and germanium have the luster associated with metals, they do not conduct heat and electricity well. These elements are used primarily in the manufacturing of solar cells and computer chips.

1.7 Properties of Groups of Elements

The important groups of atoms shown on the periodic table are listed on the following pages.

Group 1A-- The alkali metals: Excluding hydrogen, these atoms are in the far left vertical row. Francium, Fr, (87) is radioactive and very rare. These metal elements are very reactive in general and tend to oxidize easily (lose an electron) to obtain the noble gas arrangement. The most reactive is cesium.

Group 2A-- The alkaline earths: These are metals which include calcium, magnesium and barium. These metals are a bit less reactive than the alkali metals and form compounds by losing two electrons to obtain the noble gas configuration.

Groups 3B through 2B-- The transition metals: The well-known metals in this series have variable properties and defy typical group characteristics by losing a varying number of electrons. Chromium is a good example–it exists in three common atomic forms–as the familiar plating we see on automobile bumpers and the like; in a relatively innocuous trivalent state (Cr^{+3}); and as a hexavalent ion (Cr^{+6}) which is both a strong oxidizer and carcinogenic.

Group 7A-- The halogens: Also known as the "salt-formers," elements in this series are quite reactive and tend to form compounds with metals by gaining an electron to obtain the noble gas arrangement. Individual members of this class are discussed below. The reactivity trend is opposite that of the alkali metals. Fluorine is the most reactive in the series while iodine is the least.

Group 8A-- The noble gases: Also known as "Inert" gases, atoms which belong to this family are considered to be essentially non-reactive. The arrangement of the electrons, protons, and neutrons is very stable. When elements form compounds with other elements, they try to attain the noble gas electron configuration.

Hazardous Elements

There are a few hazardous materials which are found in their elemental states which you should know about:

Hydrogen--This element is the smallest atom known. It exists in nature as a molecule of two hydrogen atoms, or H_2. It is odorless, colorless and tasteless. It is also extremely flammable and burns with a colorless flame. It is usually transported as a cryogenic liquid, or in highly compressed form because it takes up less space.

Helium--This is also a gas, however, it is almost totally unreactive compared to hydrogen. It does not burn at all. Because it is unreactive, it is called a "noble gas." Bulk quantities are transported in cold, liquid form similar to hydrogen.

Magnesium--A metal which is silver in color which can burn with a very bright light. For this reason it is often used as an additive to fireworks and highway flares.

Sulfur--This element is a solid yellow powder which can burn to give off choking fumes. Even in solid from, it reacts readily with certain metals.

Bromine--This is a red liquid which smells like the chlorine in a swimming pool. It is corrosive, toxic, and produces a highly-volatile reddish-brown vapor.

Mercury--Most of us have seen the silvery liquid called mercury. Mercury and most mercury-containing compounds are toxic. Mercury is one of only two metals which is liquid at room temperature. It has been widely used in thermometers, switches, and lighting. Mercury amalgams in teeth fillings have been questioned as potential health hazards.

Iodine--This is a purple solid which gives off purple-red vapors. It is corrosive and toxic. Iodine is insoluble in water but is soluble in alcohol. A 3% mixture of iodine in alcohol and water is called "tincture of iodine".

Chlorine--Two atoms of this element form a diatomic molecule which is a yellow-green gas at room temperature. Chlorine is toxic, corrosive, and an oxidizer. A very widely-used compound. Numerous emergency response personnel are injured or killed by chlorine releases every year. Most of us have smelled this element at one time or another.

Fluorine--The most reactive of all the elements; this pale yellow gas is similar to chlorine. Fluorine is a very potent oxidizing agent.

Oxygen--A gas which is often problematic because it supports combustion and causes oxidation of nearly all metals. Required for most living organisms, it comprises about 21% of our atmosphere.

Nitrogen--A odorless, colorless, and tasteless gas which we breathe everyday because it comprises 78% of the atmosphere. Rarely a dangerous gas, it is often transported in the cold liquid form, where it is a cryogenic hazard. If it displaces the oxygen from an area, it can cause asphyxiation.

Lead--We have all seen heavy lead fishing sinkers. It is a heavy grey metal which is also toxic. The most commonly encountered form of lead is in paint and aviation gasoline. Equipment and machinery subjected to outdoor exposure including ships and airplanes are typically painted with weather resistant lead-based paint. Recent scientific studies have demonstrated that the highest atmospheric concentrations of lead occur in the first 48 hours of paint drying and pregnant women should avoid these places. Sandblasting and grinding also increase airborne lead concentrations. Lead-based paint is of great concern in older homes particularly where children are present. Lead abatement will be the asbestos of the 1990's.

Sodium--Is a silver-colored and very soft element. It is quite reactive when exposed to moisture. When freshly cut sodium has a brilliant shine, however it quickly forms a dry sodium hydroxide protective film which dulls the surface and "protects" the metal. Most often it is stored in an organic solvent such as kerosene which prevents exposure to air. Sodium reacts violently with water, starting fires and exploding. A walnut size chunk is enough to blow off your hand. A piece the size of a small pea will explode like a firecracker in water. Ionic sodium (Na^+) is an essential cellular process mineral.

Potassium--More reactive than sodium but similar in its other physical and chemical properties.

Gold and Silver--These are not often encountered in hazardous materials however, in ionic forms, these elements can be toxic and corrosive. Some new cancer-fighting compounds contain gold salts. These are, needless to say, generally beneficial to man.

1.8 The Halogens—Special Elements

The word halogen is derived from the Greek *hals*, meaning salt. The term *gen* refers to the start or origin; thus halogen means to originate from salt. What exactly are halogens?

The Halogens are the elements listed in group VII A of the Periodic Table of the Elements. These five elements: Fluorine, chlorine, bromine, iodine, and astatine are inherently chemically reactive and will combine with other elements to create literally millions of compounds. Their reactivity is due to their atomic configuration.

Atomic Structure of the Halogens

Excepting nuclear fusion and fission, all chemical reactions involve electrons. Atoms are configured such that electrons orbit the nucleus in energy shells—a familiar schematic is depicted in Figure 1. Only the electrons in the outermost or *valence* shell actually participate in the reaction. There are only three possibilities for these valence shell electrons—gain, lose, or share. The ideal electron configuration for most elements is to have eight electrons in the valence shell. Each of the halogens has only seven electrons in its valence shell. This creates an energy imbalance resulting in a strong attracting force causing these elements to "steal" and electron from another source—a chemical reaction known as **oxidation**. Fluorine's atomic structure is the smallest in the family since it has the fewest number of protons, neutrons, and electrons.

The distance from the nucleus to the outermost electrons is therefore smallest and the attractive force greatest. In fact, fluorine is the most reactive of all the elements! The remaining elements of the halogen family are also quite reactive. Fluorine, chlorine, bromine, and iodine are common constituents of innummerable compounds. Astatine is extremely rare. The name comes from the Greek *A-statos* meaning not-lasting. Astatine is a radioactive element which disintegrates very rapidly. (The most common istope has a half-life of only 0.0006 sec!)

Let's examine the remaining members of the halogen family in more detail:

Fluorine exists naturally as a pale yellow diatomic gas with a pungent odor. It is highly toxic, corrosive, and a strong oxidant. The P.E.L. is only 0.1 ppm. However, fluorine is a very beneficial element: Teflon®, polytetrafluoroethylene, is a nearly inert, highly heat and chemically-resistant material. Fluoride toothpastes help prevent tooth decay. Hydrofluoric acid is used to etch glass.

Chlorine is a greenish-yellow gas also with a pungent odor. Although not as reactive as flourine, it is a strong oxidizing agent, and is both toxic and corrosive. When one refers to a halogenated compound, more often than not the halogen is chlorine. Chlorine is used worldwide as a bacterial control agent in drinking water, swimming pools, and wastewater treatment plants. Chlorine is the active ingredient in laundry bleach and many toilet bowl cleansers. Chlorinated hydrocarbons are ubiquitous—methylene chloride, tricholorethylene, chloroform, polychlorinated biphenyls—to name a few.These materials, like all halogenated compounds, do not readily biodegrade, exhibit toxic properties, and are generally non-flammable. Chlorine has a P.E.L. of 0.5 ppm.

Bromine is a reddish-brown liquid also with a pungent odor. It is highly corrosive and toxic. Although not classified as an oxidizer by D.O.T., contact with combustible materials may cause ignition. The P.E.L. is 0.1 ppm. Bromine is used primarily in the production of ethylene dibromide (EDB), an anti-knock agent for gasoline. Other uses include bleaching, water purification, pharmaceuticals, dyes, and photography.

Iodine is a heavy, grayish-black solid having a metallic luster and a characteristic odor. The crystals readily sublime forming a violet vapor.

These vapors are toxic; the P.E.L. is 0.1 ppm. Iodine is the least reactive of the halogens but is not uncommon. Its many uses include dyes, antiseptics, food and feed additives, water treatment, and medicinal soaps.

Spotlight—Properties of the Halogens

Because of their strong electronegativity, halogen atoms bind to other atoms more tightly than any of the other elements. Their presence in a molecule also decreases the relative flammability but results in an increase in the relative toxicity. Methane (CH_4), for example, is a highly- flammable, non-toxic gas. Methylene chloride (CH_2Cl_2) is a non-flammable, toxic liquid with a P.E.L. of 100 ppm. Halogenated compounds have become one of the primary toxic pollutants of drinking water. The presence of chlorine (an excellent disinfectant) in wastewater can combine with organic materials and produce certain trihalomethanes, notably chloroform ($CHCl_3$).

Chlordane, Dioxin, Polychlorinated Biphenyls (PCBs), Trichloroethylene (TCE), and Chloroform are just a few examples of compounds whose toxicity and persistence in nature threaten both our health and our environment.

Halogen	**Fluorine**	**Chlorine**	**Bromine**	**Iodine**
Appearance and odor	Pale yellow gas pungent odor	Greenish-yellow pungent odor	Dark reddish-brown liquid	Grayish-black solid; vapors are violet
Boiling Pt. °F	- 306	-30	137	365
Vapor Density	1.3	2.45	5.32	8.76
Reactivity	High	Moderate	Moderate	Low
Hazardous Properties	Highly toxic, very corrosive, strong oxidizer	Highly toxic, strong oxidizer	Highly toxic, corrosive slight oxidizer	Highly toxic
Shipping Label	Poison, and Oxidizer	Non-Flammable Gas and Poison	Corrosive Liquid	Poison
PEL	0.1 ppm	0.5 ppm	0.1 ppm	0.1 ppm

Table 2. The Properties of the Halogens

Additional Concerns of the Halogens

Controlling wastewater discharges and landfilling of chlorinated compounds has been a major impetus of the USEPA since the passage of the Hazardous and Solid Waste Amendments Act (HSWA) in 1984. The preferred method of disposal then becomes reclaimation or incineration. However, chlorinated hydrocarbons may produce both hydrogen chloride (HCl) gas which is highly corrosive, or phosgene ($COCl_2$), a highly poisonous gas, as byproducts. Commercial incinerators have emission controls such as electrostatic precipitators, to prevent the discharge of these airborne contaminants.

Unfortunately, these same byproducts may be formed when chlorinated plastics, such as PVC, burn. These gases can be fatal if inhaled.

Another pressing environmental concern created by halogenated compounds is the degradation of stratospheric ozone. One type of halogenated compound, chloroflurocarbons (CFCs) have been identified as a primary causative agent for this depletion. If not controlled immune systems may become less effective, and skin cancers rates will certainly increase.

Certain halogen compounds may also be used to manufacture chemical weapons. The 1991 war with Iraq re-introduced the world to the threat of chemical warfare. These weapons are relatively inexpensive and easy to manufacture. Among the chemicals used for this purpose are: phosgene, cyanogen chloride, trichloronitromethane, phosphorus trichloride, and sulfur dichloride.

Chemists have managed to synthesize thousands of new halogenated chemicals. The very properties that made these materials useful—non-flammability, stability, and, in some cases, increased toxicity—now present a challenge for the 1990's. Replacement of CFCs, substitutes for current degreasing solvents, adequate incineration capacity, and new and more cost-effective treatment strategies are all significant challenges for the Environmental Chemists of the 1990's.

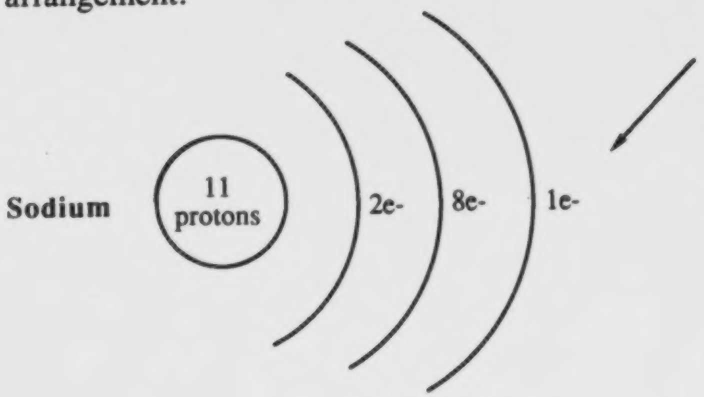
Chapter 2. Bonding in Molecules-An Introduction to Inorganic Chemistry

2.1 Electronic Configuration

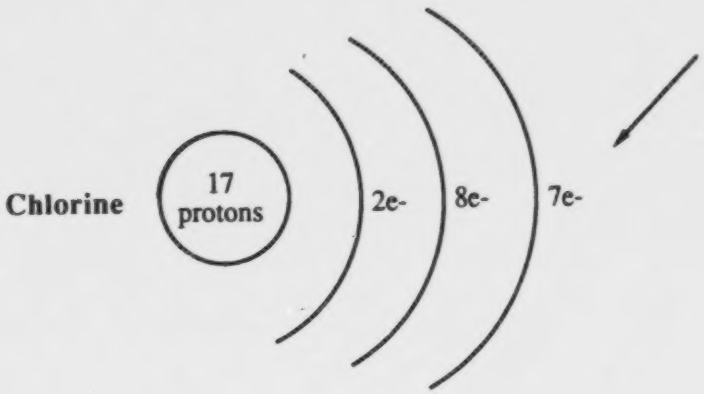
All elements have an electronic configuration and this is what makes each behave differently in bonding and reactivity. In this chapter we will see how atoms combine to make molecules and what types of bonds are possible. In all bonds we need to be concerned about electrons, because these are what joins the atoms.

2.2 Ionic Bonding and Covalent Bonding

Bonding configurations are most stable when the outermost electron shells are filled. This electron configuration is the same as the noble gas arrangement.



must lose 1 electron to chlorine to gain noble gas stability



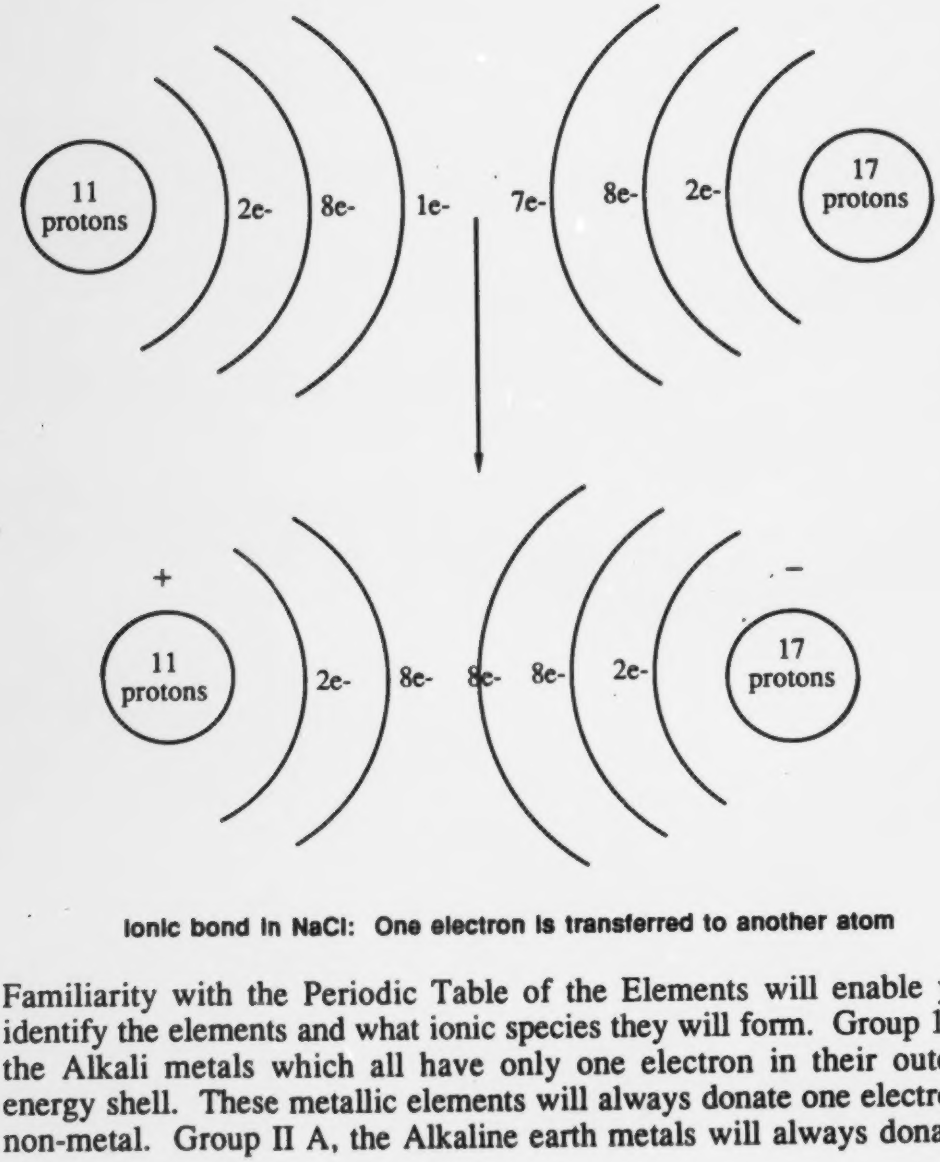
must gain 1 electron from sodium to obtain noble gas stability

For example, sodium, which has one electron in its outer energy orbit or valence shell, is very unstable. To acquire the "noble gas stability" sodium must lose one electron such that its electron configuration is now the same as neon. However, this creates a charge imbalance since there is now one more proton in the nucleus than there are electrons in the atom. The net result is a positively charged *ion* written as Na^+ or sometimes as Na^{+1}.

On the other end of the periodic table in the halogen family (VIIA) is chlorine. Chlorine has seven electrons in its outer energy shell and is therefore unstable in the monoatomic (single atom) state. In fact chlorine cannot easily exist in this electron configuration: It must either gain one electron, creating a negatively-charged particle (ion) written as Cl^-, or combine with another chlorine atom to from a diatomic chlorine gas molecule (Cl_2). The process of gaining the electron gives chlorine the "noble gas stability" of argon. The bonds formed when these oppositely-charged particles combine is called an *ionic bond*. This is the bond that forms when chlorine ions (Cl^-) and sodium ions (Na^+) join together. Sodium "gives up" its unwanted electron to chlorine who is happy to accept it. Each helps the other achieve noble gas stability.

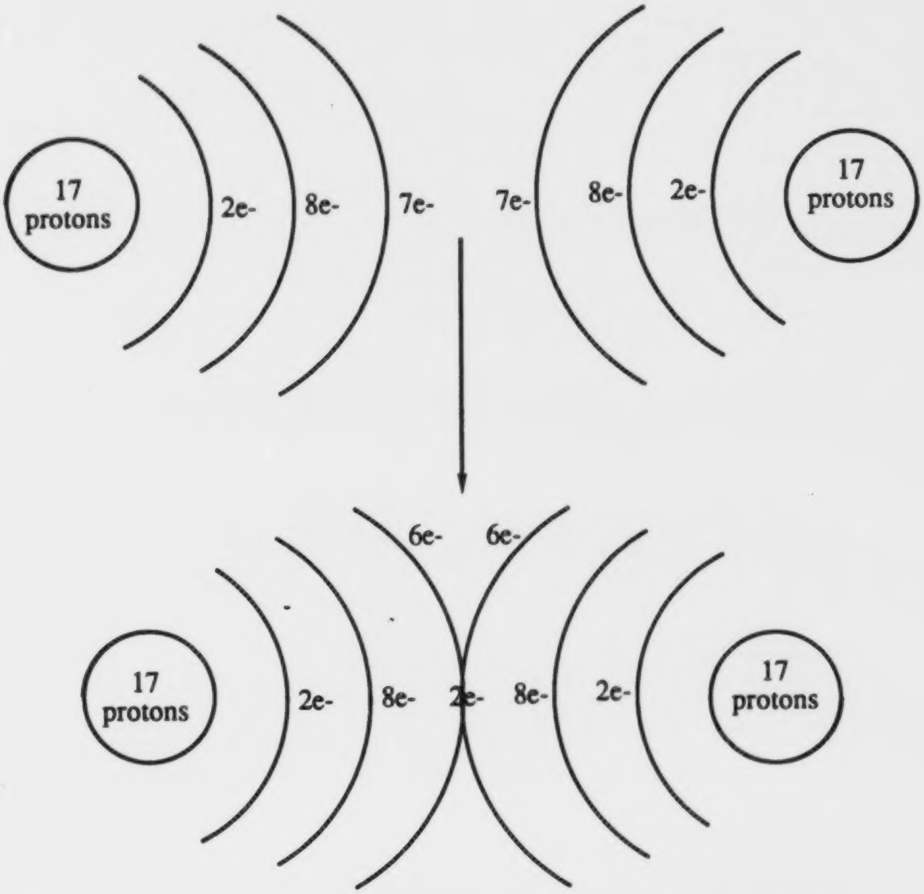
You should understand that in order to form an ion, an atom must be either an electron donor or acceptor. That is, atoms can only gain an electron from another atom which donates it. Sodium chloride (NaCl), or table salt, is one example of this type of bonding. NOTE: Ionic bonding **always** occurs between a metal (sodium) and a non-metal (chlorine) to form a salt (NaCl).

Elements are comprised of electrons, neutrons, and protons. The center of an atom, or *nucleus* , consists of protons (positively-charged particles) and neutrons which have mass but no charge. Orbiting the nucleus are electrons (negatively-charged particles). For a stable atom, the number of electrons and protons in a given element must be equal. The number of neutrons however, can and does vary creating *isotopes*. An isotope is a different form of the same element with a higher atomic weight than its parent form. For example deuterium (with one neutron) and tritium (with two neutrons) are isotopes of hydrogen. Several isotopes, like trititum, are radioactive-their atoms spontaneously disintegrate into other elements. The atomic number of an element tells you the quantity of protons (and electrons) it contains. Bonding configurations are most stable when the outermost electron shell is filled to capacity. For example, sodium which has one electron in its outer shell, is inherently unstable. To acquire atomic stability, sodium tends to lose this one electron creating a charge imbalance since there are now more protons than electrons. The net result is a positively charged *ion* , written as Na^+. (Sodium can only form an ion if another element is willing to accept this electron.)



Ionic bond in NaCl: One electron is transferred to another atom

Familiarity with the Periodic Table of the Elements will enable you to identify the elements and what ionic species they will form. Group 1 A are the Alkali metals which all have only one electron in their outermost energy shell. These metallic elements will always donate one electron to a non-metal. Group II A, the Alkaline earth metals will always donate two electrons; Groups V A, VI A, & VII A (the Halogens) will gain 3, 2, and 1 electrons respectively. Note that the group or family numbers indicate the number of electrons in the outermost orbit. Elements within each group exhibit similar physical and chemical characteristics--**periodicity**--hence the Periodic Table.

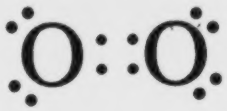


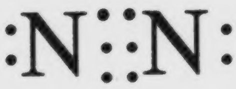
Covalent Bond: Two electrons are now shared by each atom

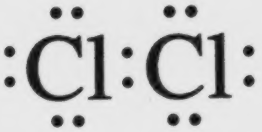
Covalent bonding will be encountered later in the chapters dealing with organic chemistry. In these bonds, the electrons are shared between atoms and no electron transfer occurs. Some inorganic chemicals form covalent bonds when they come "two to a package" that is as a diatomic molecule. There are seven elements which exist naturally only as diatomic molecules. These are bromine (Br_2); iodine (I_2); nitrogen (N_2); chlorine (Cl_2);

hydrogen (H_2); oxygen (O_2); and fluorine (F_2). An easy way to remember these is the mneumonic "BrINClHOF". These diatomic elements share outermost electrons such that each atom "believes" the energy shell is filled. This imparts the "noble gas stability" intrinsic to these substances. A dot formula representing the electron configuration for a few of these is shown below:

$H:H$







Let's summarize the differences between these two bonds: In ionic bonds, an extra electron (or electrons) are "owned" by one atom (the donee) which were "taken" from another atom (the donor). This produces an ionic bond between the atoms. In general, metals tend to lose electrons and become *cations* (positively-charged particles) while non-metals tend to gain electrons and become *anions* (negatively-charged particles). In covalent bonds, electrons are shared equally between atoms so that each atom "appears" to fill its outermost electron shell thus achieving noble gas stability. Covalent bonding occurs between the atoms when non-metals combine with non-metals to form diatomic molecules or compounds.

The process in which electrons are gained or lost is called *oxidation-reduction* or "redox". When one atom gains (takes) an electron from another atom, it is *reduced*. The atom which lost the electron(s) is *oxidized*. Atoms which can easily take electrons, such as fluorine and oxygen are called *oxidizing agents or oxidizers*. Those atoms which most readily donate electrons are called *reducing agents*. A simple sentence pneumonic to help you remember electron movement in oxidation-reduction is: *Leo the lion goes Ger*. Leo = loss of electrons-oxidation; Ger = gain of electrons-reduction.

2.3 An Introduction to Inorganic Chemistry

Although there are many disciplines in the field of Chemistry: Biochemistry, Physical Chemistry, Analytical Chemistry, etc.; these are all subdivisions of two major divisions in Chemistry: **Inorganic Chemistry** and **Organic Chemistry**. Inorganic Chemistry deals with the study of substances that do not contain carbon atoms with the exception of a few compounds.

Inorganic chemistry centers on the study of atoms, molecules, and elements including properties related to chemical bonding, electrochemistry, and acid-base reactions. In this section an introduction to we will examine some of these concepts as they relate to the study of hazardous materials.

In our study we will be concentrating on *chemical reactions*, that is those that involve electron transfer or sharing. The other type is a nuclear reaction which involves forcibly changing the nucleus of an atom either by breaking it apart *(fission)* or by combining subatomic particles *(fusion)* to form a new element or create usable energy. As these nuclear reactions are typically confined to the stars, nuclear reactors, and atomic weapons, we will concentrate on the chemistry of the atoms.

2.4 Inorganic Elements—All Except Carbon

Elements are the simplest form of matter; that is, elements consist of only one type of atom (containing protons, neutrons, and electrons) which can only be subdivided by a nuclear reaction. Many of the elements are readily familiar—hydrogen, helium, aluminum, iron, gold, silver, lead, mercury, to name just a few. While scientists have now characterized 107 elements, we will confine our study to only 48 of these elements in our study of hazardous materials, since these comprise the majority of commonly encountered hazardous materials.

Many elements dissolve in water to form what is called a *solution*. In fact any substance, compound, or mixture in combination with water is known as a solution. This aspect of hazardous materials is very important since many hazardous materials are found as solutions and must be compatible with other materials present in the solution otherwise an undesirable reaction may occur which can be detrimental.

Table 3 / 48 Elements and Their Symbols

Hydrogen	H	Helium	He	Rubidium	Rb	Strontium	Sr
Lithium	Li	Beryllium	Be	Iodine	I	Xenon	Xe
Boron	B	Carbon	C	Cesium	Ce	Barium	Ba
Nitrogen	N	Oxygen	O	Radon	Rn	Chromium	Cr
Fluorine	Fl	Sodium	Na	Manganese	Mn	Iron	Fe
Magnesium	Mg	Cadmium	Cd	Cobalt	Co	Nickel	Ni
Aluminum	Al	Silicon	Si	Copper	Cu	Zinc	Zn
Phosphorus	P	Sulfur	S	Gold	Au	Silver	Ag
Chlorine	Cl	Argon	Ar	Platinum	Pt	Tin	Sn
Potassium	K	Calcium	Ca	Antimony	Sb	Mercury	Hg
Arsenic	As	Selenium	Se	Lead	Pb	Radium	Ra
Bromine	Br	Krypton	Kr	Uranium	U	Plutonium	Pu

2.5 Inorganic Compounds

Inorganic compounds are those in which most of the bonding is ionic in nature. A simple experiment can be performed to determine whether a compound is composed of ions or atoms: Connect copper wire electrodes to the negative and positive terminals of a dry cell battery and place these into a container of distilled water, using a conductivity meter, check the current. It will read zero! Now add a small amount of NaCl; instantly, as the salt dissolves, a current begins to flow. This is due to the flow of electrons from one electrode to the other across the ions. Try this experiment again with common sugar (sucrose) and you will get a reading of zero even after dissolving the sugar because the elements are covalently bonded. The bottom line is that *ions conduct electricity* because they are charged.

For an Elementary Experience--

C. HOPKINS CaFe

(Take it with a grain of NaCl)

Certain physical and chemical properties differentiate inorganic compounds. Elements are usually classified as inorganic substances although molecular bonding is covalent; i.e. the atoms share electrons rather than accepting or donating them.

2.6 Inorganic Ions

Inorganic ions can be composed on one atom, as in the case of Cl^- of Na^+, or can be composed of several atoms as in the case of the acetate ion $C_2H_3O_2^-$, or the ammonium ion NH_4^+. In this section we will look at several ions which are often found in solutions and are generally found in combination with a "counterion", an oppositely-charged ion to balance the charge and produce a neutral salt. One counterion for the ammonium ion in the chloride ion, such that a stable neutral salt, $NH_4^+Cl^-$ (ammonium chloride) is formed.

Metals, including the transition metals, tend to produce *cations*. Like Na^+, the other alkali metals in Group IA tend to lose one electron to attain the noble gas configuration: lithium Li^+, potassium K^+, and cesium Cs^+. Hydrogen, a nonmetal, is placed in this category because it loses an electron to become H^+ just like the metals below it on the Periodic Table. We will study the important chemistry of H^+ when we discuss acids in a later chapter. The next group is IIA, the alkali earth metals which must lose two electrons to form a noble gas ion. This group includes beryllium Be^{++}, magnesium Mg^{++}, calcium Ca^{++}, strontium Sr^{++}, barium Ba^{++}, and radium Ra^{++}.

+1 Ions of Group IA: The Alkali Metals

Li^+	pharmaceuticals, batteries
Na^+	salt
K^+	salt substitutes
Cs^+	electronic eyes

+2 Ions of Group IIA: The Alkaline Earth Metals

Be^{++}	lignting sources, "space-age" metal alloys
Mg^{++}	ignitions, flares
Ca^{++}	bones, teeth, critical ion in body systems
Sr^{++}	pyrotechnics
Ba^{++}	medicine
Ra^{++}	radiology

The transition metals are a bit tough to put into a decent order since these atoms can exist in more than one ionic state. Many of these transition metals are well-known and important in our society. Many also are found in hazardous materials and hazardous wastes.

+1 Ions of the Transition Metals

Cu^{+}	copper (I) or cuprous ion
Ag^{+}	silver (photographic film)
Au^{+}	gold

+2 Ions of the Transition Metals

Cu^{++}	copper (II) or cupric ion
Fe^{++}	iron (II) or ferrous ion
Pb^{++}	lead (II) or plumbous ion
Hg^{++}	mercury (II) or mercuric ion
Ni^{++}	nickel (II) or nickelous ion
Sn^{++}	tin (II) or stannous ion
Zn^{++}	zinc

+3 Ions of the Transition Metals

Cr^{3+}	chromium (III) or chromous ion
Fe^{3+}	iron (III) or ferric ion

+4 Ions of the Transition Metals

Sn^{4+}	tin (IV) or stannic ion
Pb^{4+}	lead (IV) or plumbic ion

Returning to the Periodic Table to the right of the transition metals, we have the elements in Groups IIIA—VIIA. Each group contains atoms which either gain or lose electrons to try to achieve the noble gas configuration.

+3 Ions of Group IIIA

Al^{3+}	aluminum
Ga^{3+}	gallium

+4 Ions of Group IVA

Sn^{4+}	tin (IV) or stannic ion
Pb^{4+}	lead (IV) or plumbic ion

-3 Ions of Group VA

N^{3-}	nitride ion
P^{3-}	phosphide ion
As^{3-}	arsenide ion

-2 Ions of Group VIA

O^{2-}	oxide ion
S^{2-}	sulfide ion

-1 Ions of Group VIIA: The Halogens

F^-	fluoride ion
Cl^-	chloride ion
Br^-	bromide ion
I^-	iodide ion

In addition to the ions listed above, a number of ions are "polyatomic", in other words, they contain several ions and collectively have a charge on the entire species. An example is the ammonium ion $NH4^+$ which we saw earlier. These ions are more difficult to define because the majority of the atoms in the species are covalently bonded.

+1 Polyatomic Ions

NH_4^+	ammonium ion

-1 Polyatomic Ions

$C_2H_3O_2^-$	acetate ion
HCO_3^-	bicarbonate ion
HSO_4^-	bisulfate ion
ClO_3^-	chlorate ion
CN^-	cyanide ion
$H_2PO_4^-$	dihydrogen phosphate ion
OH^-	hydroxide ion
ClO^-	hypochlorite ion
ClO_2^-	chlorite ion
ClO_3^-	chlorate ion
ClO_4^-	perchlorate ion
NO_3^-	nitrate ion
NO_2^-	nitrite ion
MnO_4^-	permanganate ion

-2 Polyatomic Ions

CO_3^{2-}	carbonate ion
$Cr_2O_7^{2-}$	dichromate ion
SO_4^{2-}	sulfate ion

-3 Polyatomic Ions

PO_4^{3-}	phosphate ion

2.7 Inorganic Salts

Most of these inorganic ions form salts by pairing the charges together to form a neutral compound. When forming salts, several things must be considered: First, determine the charges on the individual ions from the charts above; second, the charges on the anion(s) must equal the charges on the cation(s) such that there is no charge on the compound (salt); third, write the symbol for the positive ion on the left and the negative ion on the right without charges indicated; finally, use parentheses to indicate the number of polyatomic ions present in the compound. For example calcium hydroxide--$Ca(OH)_2$. Some common salts are shown in the table below.

2.8 Some Common Salts and their Uses

NAME	FORMULA	COMMON NAME	USE
aluminum acetate	$Al(C_2H_3O_2)_2$	Burrow's solution	astringent
aluminum sulfate	$Al_2(SO_4)_3$	Alum	water treatment
ammonium carbonate	$(NH_4)_2CO_3$	smelling salts	
barium sulfate	$BaSO_4$		X-rays
calcium carbonate	$CaCO_3$	limestone	antacid
calcium hydroxide	$Ca(OH)_2$	slaked lime	water treatment, etc.
calcium oxalate	CaC_2O_4		urine stone
calcium oxide	CaO	unslaked lime	cement, concrete
calcium sulfate	$CaSO_4$		plaster casts
calcium silicate	$CaSiO_4$	gypsum	construction
magnesium hydroxide	$Mg(OH)_2$	milk of magnesia	laxative/water treatment
magnesium sulfate	$MgSO_4$	epsom salts	laxative
potassium chloride	KCl	low sodium salt	salt substitute
potassium hydrogen tartrate	$KHC_4H_4O_6$	creme of tartar	baking
potassium iodide	KI		antifungal
potassium permanganate		$KMnO_4$	sterilizer
potassium nitrate	KNO_3	saltpeter	antiseptic
silver nitrate	$AgNO_3$		antiseptic/photography
sodium bicarbonate	$NaHCO_3$	baking soda	cooking/antisepsis/other
sodium bromide	$NaBr$		sedative
sodium carbonate	Na_2CO_3	washing soda	cleaner
sodium chloride	$NaCl$	table salt	flavoring
sodium hydroxide	$NaOH$	lye	unclog drains
zinc oxide	ZnO		astringent
zinc cyanide	$Zn(CN)_2$		zinc plating (galvinizing)

You should notice that the anions in the salts are often named with an *ide* ending, thus oxygen becomes oxide; chlorine, chloride; nitrogen, nitride; and so on. Note that many substances which end with *ate* or *ite are* oxidizing agents especially if there is a *per* prefix: potassium *per*mangan*ate*, ammonium *per*chlor*ate*, sodium nitr*ate*, sodium hypochor*ite*.

It is interesting to evaluate the elemental constituents in the human body. As all matter is compromised of elements, the human body must be also-a portion in the form of inorganic salts. The largest percentage of the elements in the body are bound into organic (carbon-based) compounds–the focus of the next few chapters. The elemental composition of a 70 kg (154 lb) human adult is quite interesting:

	Abundance in body	
Elements	**ppm**	**Percent of body mass**
Hydrogen, oxygen, carbon nitrogen, calcium	10,000 to 630,000	99
Phosphorus, chlorine, sodium, potassium, sulfur, magnesium	400 to 7,000	1
Iron, Zinc	25 to 50	0.01
Copper, tin, manganese, iodine bromine	1 to 10	Trace
Fluorine, molybdenum	0.2 to 0.5	Trace
Arsenic, cobalt, chromium, lithium, nickel	0.02 to 0.04	Trace
Cadmium, selenium	Less than 0.02	Trace

Chapter 3. An Introduction of Organic Chemistry

3.1 Introduction

The study of organic chemistry touches on all facets of our modern life. Its endless varieties of molecules are contained in all living matter including ourselves, animals, and plants in the form of proteins, DNA, enzymes, and sugars we contain. Excluding water, most of the remaining compounds in the body contain carbon in their structure. In fact, 99% of the human body is comprised of only five elements—carbon, hydrogen, oxygen, nitrogen, and calcium. In many ways our very heredity and memory depend on carbon molecules. Diamond, a valuable crystalline substance, is the hardest material known. Pencil leads are made of a relatively soft gray solid called graphite. Both are made of pure carbon. Fuels such as gasoline, coal, and oil were once living matter which contained carbon molecules. Medicines ranging from simple pain-killers like aspirin to complex life-saving drugs such as cyclosporin are all prepared from carbon compounds.

The study of organic chemistry involves the study of compounds made of carbon. Hydrocarbons are the backbone of most organic chemicals and, as their name suggests, contain only carbon and hydrogen atoms. Other atoms important to the study of organic chemistry are nitrogen, as found in amines (—NH_2); oxygen, as in alcohols (—OH); and halogens, as in halogenated hydrocarbons (halocarbons). In the next few chapters we will learn how to same some simple organic compounds and learn some of the hazards associated with the different classes of organic compounds.

There are several distinct differences between organic and inorganic chemicals. First, organic compounds are *nearly all flammable* and **all** will burn under the right conditions. Second, organic compounds have lower freezing points and boiling points than nearly all inorganic salts. Third, organic compounds do not conduct electricity and are mostly non-soluble.

3.2 A Review of the Basics

Before we can get down to studying organic chemistry, there are certain words which are important to understanding the field. Let us examine the vocabulary of the organic chemist:

A *functional group* is a special grouping of atoms in an organic molecule *which imparts* certain characteristics to the compound. One functional group is the alcohols (–OH); another is the amines (–NH_2); and yet another is the nitrile (–CN) group. The functional group is important for many reasons. It allows us to correctly name the compound, to predict certain physical properties, and to characterize the hazards of the material. We will be studying the *nomenclature* or the naming of a molecule as a tool to understand organic chemicals. The next several pages are organized by functional groups. The nomenclature for each functional group is a bit different so we will examine several groups.

The ruling board in organic chemistry which determines the proper name for a compound is the *International Union of Pure and Applied Chemists* or IUPAC. This group began as a collection of chemists who first met in Geneva, Switzerland in 1892. The present rules were largely developed by 1965, they are uniform and, in some situations, quite complex. This system is called *systematic nomenclàture*. These names are always scientifically correct.

Throughout our reading we will also encounter *common names*, which are still used today because they are more familiar to most people. The differences between the two name may be slight as in the case of *methyl chloride* (common) vs. *chloromethane* (IUPAC) or significant as in the case of *benzene* (common) vs. *cyclohexatriene* (IUPAC).

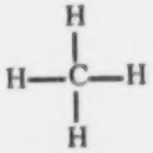
Another important distinction is the organic classification of **aliphatic** and **aromatic** hydrocarbons. Put as simply as possible, aliphatic hydrocarbons are chains of carbons atoms arranged in many different ways, e.g. straight chains, branched chains, and rings. Aromatic hydrocarbons are **all** based on the molecule benzene which we will explore in detail later in Chapter 11.

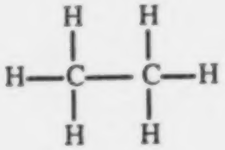
3.3 The Alkanes

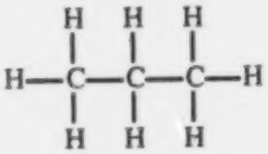
This group lacks any functional group, however, it is the basis for all the organic molecules we will be studying. These compounds are aliphatic hydrocarbons, hence the **al** in alkane. Any simple alkane contains only carbon and hydrogen atoms thus the name *hydrocarbons*. If we add up the carbon and hydrogen atoms in an alkane molecule, there will always be twice as many hydrogens (plus 2 more) as there are carbons. An alkane always fits the formula C_nH_{2n+2}, for example C_3H_8, propane. Sometimes a fragment of an alkane is named as a functional group known as an *alkyl group*. The bonds between the carbon atoms is the alkane series are single covalent bonds, i.e., they involve only one *shared* pair of electrons. As such these compounds are known as *saturated hydrocarbons*.

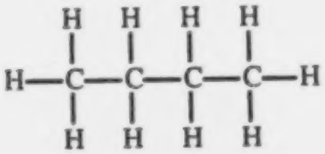
The longest backbone is critical, and it determines the name of the whole molecule. The words are Greek or Latin in origin with an "ane" ending, used for alkanes. The first thing to do when naming a compound is to locate the longest chain (of carbon atoms). This number will provide the root word for naming the compound.

Carbons	**Root Name**	**Functional Group Name**
1	Meth	Methyl
2	Eth	Ethyl
3	Prop	Propyl
4	But	Butyl
5	Pent	Pentyl
6	Hex	Hexyl
7	Hept	Heptyl
8	Oct	Octyl
9	Non	Nonyl
10	Dec	Decyl

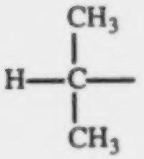

Methane CH_4


Ethane C_2H_6


Propane C_3H_8

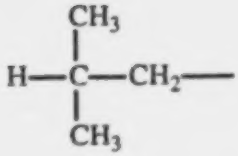

Butane C_4H_{10}

Some alkanes are named as functional groups "hanging off" of long chains which have the following common names. These have recently been adopted as IUPAC names.



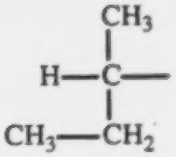
$$\begin{array}{ccc} & \mathrm{CH_3} & \\ & | & \\ \mathrm{H}- & \mathrm{C} & - \\ & | & \\ & \mathrm{CH_3} & \end{array}$$

isopropyl



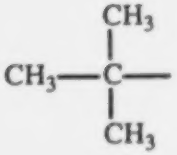
$$\begin{array}{cccc} & \mathrm{CH_3} & & \\ & | & & \\ \mathrm{H}- & \mathrm{C} & -\mathrm{CH_2} & - \\ & | & & \\ & \mathrm{CH_3} & & \end{array}$$

isobutyl



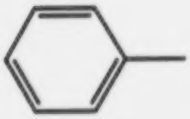
$$\begin{array}{ccc} & \mathrm{CH_3} & \\ & | & \\ \mathrm{H}- & \mathrm{C} & - \\ & | & \\ \mathrm{CH_3}- & \mathrm{CH_2} & \end{array}$$

sec-butyl



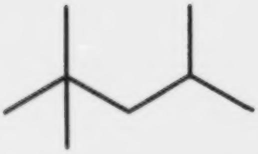
$$\begin{array}{ccc} & \mathrm{CH_3} & \\ & | & \\ \mathrm{CH_3}- & \mathrm{C} & - \\ & | & \\ & \mathrm{CH_3} & \end{array}$$

tert-butyl

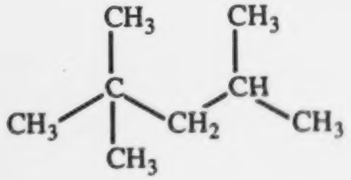


phenyl

Throughout this chapter and others we will use "chemists shorthand", where the individual carbon atoms are not shown. Instead, lines will be used to show the bonds and the C's and H's will be omitted. Assume there is a carbon at the end of each line or at any corner where two lines intersect. For example, the two structures shown below for 2,2,4-trimethylpentane are the same; only the representations are different.



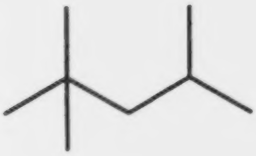
is the same as:



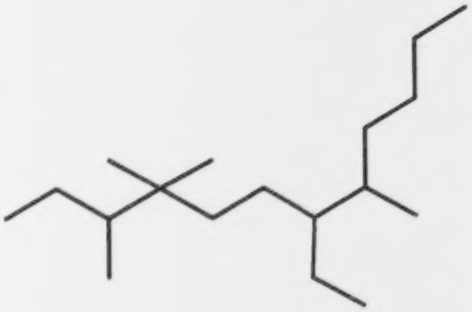
3.4 General Rules for the Nomenclature of Alkanes

Always follow these steps when you encounter a new organic molecule that you do not know the name of. The sequence of rules has been tried and true for many decades.

1. Find the longest chain and name it.

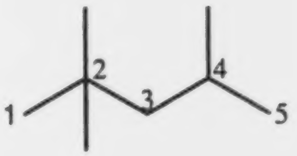


5 carbons--a pentane

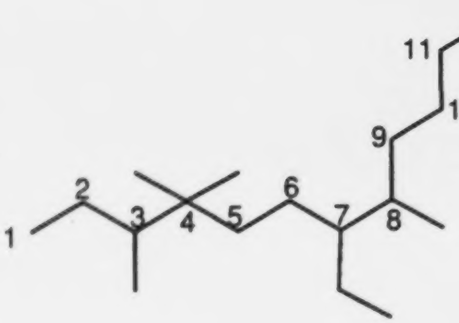


12 carbons--- a dodecane

2. Name all the functional groups on the longest chain by number, starting at the end that has the "closest" functional group.

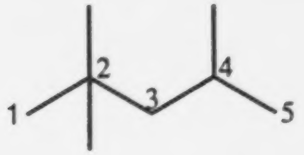


2,2,4-trimethyl

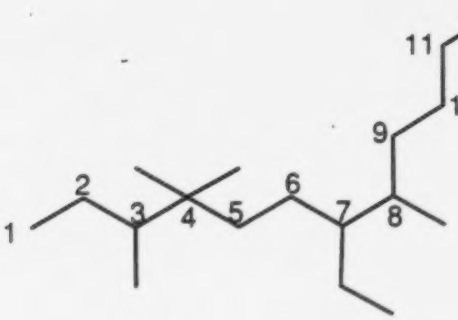


3,4,4,8-tetramethyl
7-ethyl

3. Put all the groups in alphabetical order preceding each by their number in the chain.



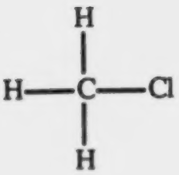
2,2,4-trimethylpentane
(iso-octane–a major component
of gasoline)

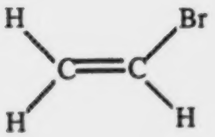


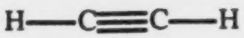
7-ethyl-3,4,4,8-tetramethyldodecane

3.5 Covalent Bonding

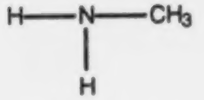
Remember that there are always four (4) bonds on carbon (sharing a total of 8 electrons) and these bonds can exist in many different forms. A single bond (one pair of electrons) may also be shared between a carbon atom and a hydrogen or halogen atom.



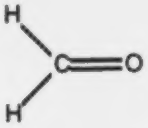




Nitrogen likes to have three (3) bonds and oxygen likes to have two (2) bonds to satisfy their respective electron configurations. Ammonia, NH_3, an inorganic compound also has only three bonds on the nitrogen atom.



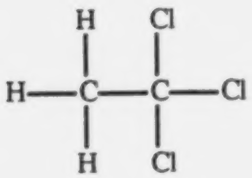
Methyl amine



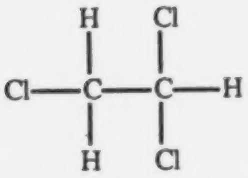
Formaldehyde

3.6 Isomers

Many organic compounds have the same molecular formula and yet a different arrangement of atoms (structure). This difference in structure may result in widespread differences in physical and chemical properties of each compound. The two structures shown below have the same identical formula–$C_2H_3Cl_3$–however, each has a different arrangement of atoms.



1,1,1-trichloroethane



1,1,2-trichloroethane

Compounds like these with the same formula but different structures are called *isomers*. Isomers typically have different boiling points, melting points and other different physical properties. In hazardous materials chemistry, although each of these compounds is likely to be similar, the hazardous properties may vary and each compound will be listed separately by CAS number. There are two guidelines to the recognition of isomers:

1. Determine the molecular formula. Isomers will have the same formula.

2. Examine the bonding arrangement. Isomers will have their atoms arranged differently while identical compounds will have the same exact bonding arrangement.

3.7 Ring Compounds

Organic compounds come in many shapes and sizes. Some exist as rings. The smallest possible size is a three-membered ring. Both the three- and four-membered rings are strained and thus contain a lot of energy which is released when these compounds are burned. The smallest-sized ring compounds are found in the gaseous state. The majority of the other common ring compounds are liquids. If these compounds are pure hydrocarbons, they will fit the formula C_nH_{2n} and contain only C and H atoms. For naming simple ring compounds, use the prefix *cyclo* and then the alkane name for the ring size. Some examples are shown on the following page.

3.8 Hazards with Alkanes

1. All of these molecules are flammable. Especially dangerous are the gases and the volatile liquids.

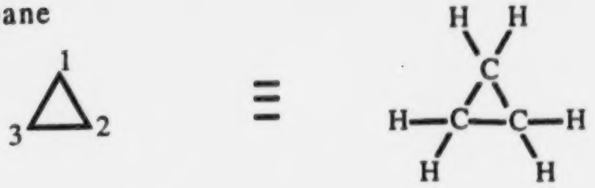
2. When burned, they give off water and carbon dioxide and remove oxygen from the air.

3. An alkane under pressure can be especially dangerous.

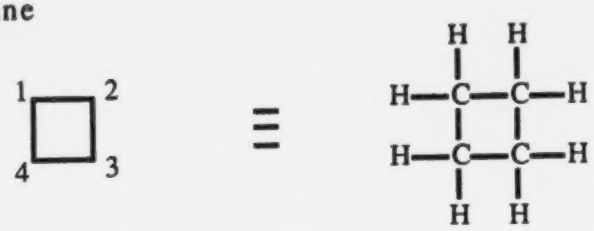
4. All of the gases can kill if enough is inhaled. These are simple asphyxiants and narcotics.

5. Some liquids, such as hexanes, are also irritants.

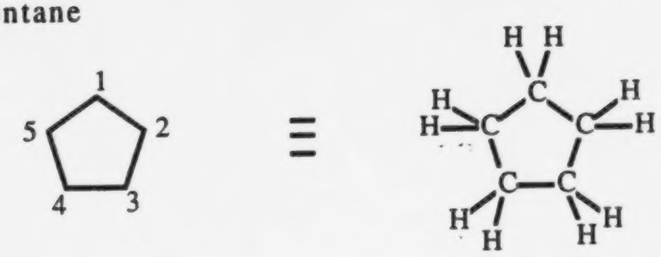
cyclopropane



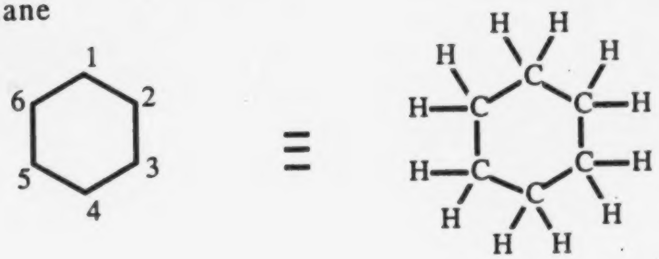
cyclobutane



cyclopentane



cyclohexane

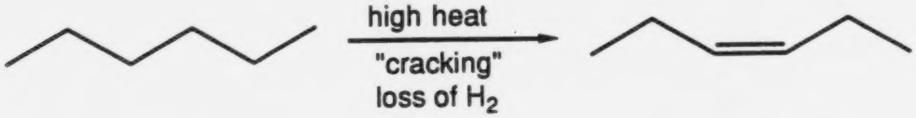


Cyclic Hydrocarbons: The Cycloalkanes

Chapter 4. Alkenes and Alkynes

Hydrocarbons containing at least one double bond are called **alkenes**. These can be in rings or in an open chain. In a similar manner, hydrocarbons containing at least one triple bond are called **alkynes** or acetylenes. Sometimes the term *unsaturated* is used to describe both classes of molecules because reactions can take place which can convert these molecules to a carbon-carbon single-bonded alkane, or *saturated* hydrocarbon. An alkene has one unsaturation (a double bond) while an alkyne has two (a triple bond).

The need for unsaturated hydrocarbons in industry far exceeds nature's ability to produce them. Industrial chemist can heat alkanes in the absence of air to very high temperatures in a process called *cracking*, to prepare them from petroleum and natural gas. In this process, an alkane splits off hydrogen, H_2, to produce each unsaturation:



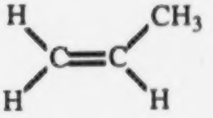
The alkene is a true functional group which fits the formula C_nH_{2n}. Alkynes, which contain a triple bond have the formula C_nH_{2n-2}.

Examples:

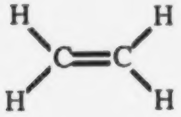
Common names:

$H-C\equiv C-H$

acetylene



propylene



ethylene

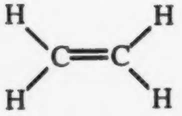
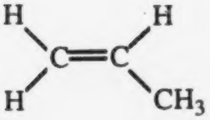
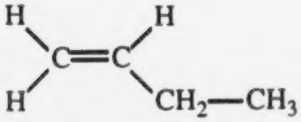
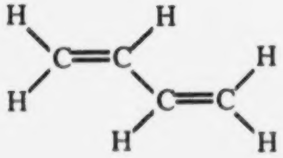
$CH_3-CH_2-C\equiv C-CH_2-CH_3$

diethylacetylene

4.1 Nomenclature

For alkenes we use the suffix "ylene" instead of the "ane" ending normally found in alk*anes* and "yne" for alkynes using the same basic Greek and Latin prefix from the Table in Chapter 3. For the IUPAC name we use "ene" endings for alkenes.

4.2 A Quick Guide to Naming Some Alkenes and Alkynes

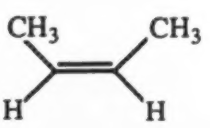
	Prefix	+	Suffix	=	Name
	eth	+	ene	=	ethene (ethylene)
	prop	+	ene	=	propene (propylene)
	but	+	ene	=	butene (butylene)
	but	+	diene	=	butadiene

Alkynes:

$H-C\equiv C-H$	eth	+	yne	=	ethyne (acetylene)
$H-C\equiv C-CH_3$	prop	+	yne	=	propyne

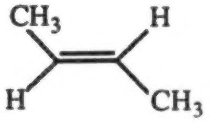
4.4 Geometric Isomers of 2-Butene

There are two other kinds of isomers found in alkenes–these are the geometric isomers. Similar to the isomers we learned about in Chapter 3, these have different boiling points and melting points and other physical characteristics. They have different hazard characteristics and different listings in the chemical literature. Notice that the two methyl groups are the largest groups on the alkene. They are on the same side in *cis*-2-butene and on opposite sides in *trans*-2-butene.



cis-2-butene
bp = 4°C
mp = -139°C

is not the same as:

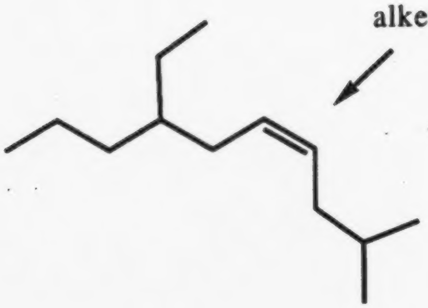


trans-2-butene
bp = 1°C
mp = -106°C

Using what we now know about cis and trans isomers and alkene nomenclature, let's try a more complex example.

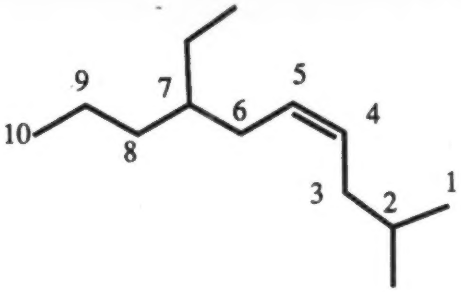
4.4 General Rules for the Nomenclature of Alkenes

1. Find the longest chain that contains the alkene functional group.



2. The location of the alkene is indicated by number. The numbering of the chain starts with the end closest to the alkene.

In cycloalkenes, carbons 1 and 2 are always indicative of the position of the alkene.



7-ethyl

2-methyl

double bond is in the 4-position--

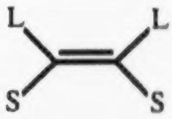
4-decene

3. Lastly, add the substituents by number and alphabetize as before.

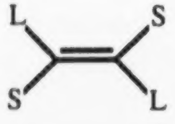
The correct name is: 7-ethyl-2-methyl-4-decene

4.5 Cis-Trans Designations

4. Now we apply geometric isomerism to our compound. Remember, if the two largest functional groups are on the same side of the alkene, they are cis, if they are on opposite sides, they are trans.

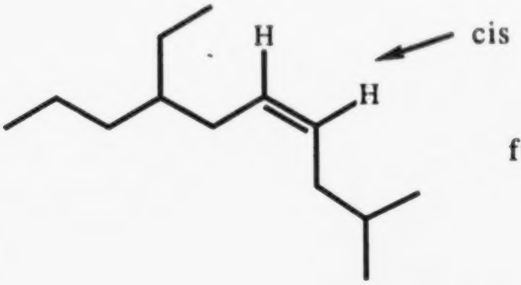


vs.



L=large group

S=small group

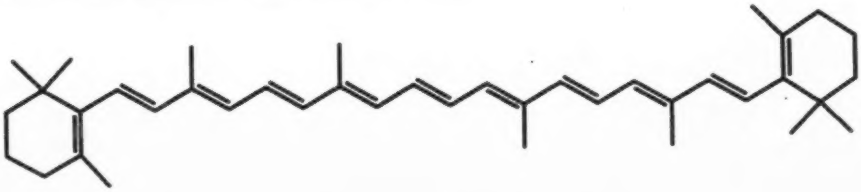


full name: cis-7-ethyl-2methyl-4-decene

Spotlight—Margarine and Butter

Did you have pancakes this morning? If you did, you may have used one of these fats along with a nice portion of hot syrup. What could be more tasty for breakfast? Butter is made from cream by a process called *churning*, which simply allows air into the butterfat and causes it to harden. The liquid left behind is called the buttermilk, another delightful snack.

Margarine was originally designed as a butter substitute in 1859. The root word, *margaron*, comes from the Greek word for pearl. Unfortunately the original margarine was made from milk, chopped cow udder, and beef tallow. Today margarine is made from products from the petroleum industry. One of the natural coloring agents which gives butter and margarine a yellow color is *carotene*, which contains many unsaturations or alkenes. Note the word carotene has the suffix *ene*.



Carotene

4.6 Hazards with Alkenes and Alkynes

1. These are very similar to those of alkanes, i.e. they are very flammable.

2. These compounds can also undergo polymerization and can harden and/or expand at an alarming rate in the presence of initiators. Considerable heat can be generated.

3. Most of these low molecular weight compounds are asphyxiants and cause narcosis and unconsciousness.

4. Acetylenes or alkynes can explode, especially in the presence of halogens.

5. In the presence of metals such as silver, copper, mercury, or magnesium, explosive metal acetylides can form.

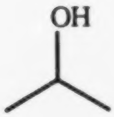
Chapter 5. The Alcohols

Most functional groups contain an oxygen atom in some form. The alcohols are no exception. Many alcohols may be familiar to you already. These include rubbing alcohol, wood alcohol, and drinking alcohol or grain alcohol. The simplest alcohol is *methanol* or *methyl alcohol*. It is also called wood alcohol because up until 1926 it was prepared entirely from the distillation of wood products. The next higher alcohol is called *ethanol* or *ethyl alcohol* which comes from the fermentation of sugars. It is also the common alcohol in "gasohol", a 10% mixture with gasoline found at many service stations.

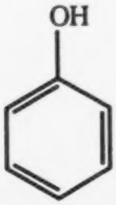
The hazard properties of these compounds vary widely but most members of this class are poisonous. Even ethanol, the grain alcohol found in beer and vodka can kill if enough is ingested. Many simple alcohols pass right through the skin and can enter the body this way.

This functional group is an -OH and it is sometimes called the hydroxy or hydroxyl group. It imparts polarity (charge) on the molecule and indeed, some of the lower molecular weight alcohols are water soluble. This group represents the first oxidation state of an organic molecule (the addition of oxygen to the alkane backbone).

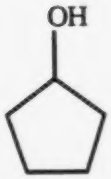
Examples:



2-propanol
(isopropyl alcohol)



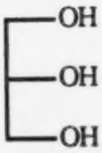
phenol
(carbolic acid)



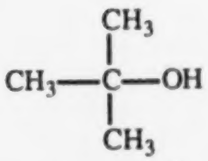
cyclopentanol

$CH_3{\cdot}CH_2\text{—}OH$

ethanol
ethyl alcohol



glycerol



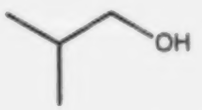
$$CH_3\text{—}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\text{—}OH$$

tert-butyl alcohol

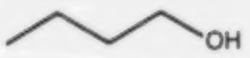
5.1 General Rules for the Nomenclature of Alcohols

Use these guidelines for naming alcohols:

1. Name the alcohol with the suffix "ol" by using the Greek or Latin name on the table in Chapter 3.Notice that the longest chain that contains the -OH group.

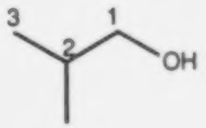


a propanol

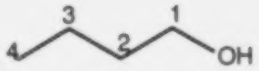


a butanol

2. Number the chain with the -OH at the lowest position or at the end nearest the number 1.

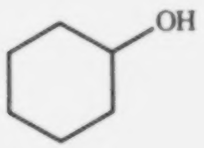


2-methylpropanol
(isoamyl alcohol)



1-butanol

3. Cyclic alcohols have a "cyclo" prefix

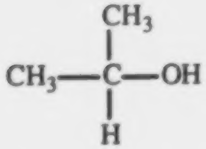


cyclohexanol

4. For common names, we use the Greek or Latin prefix for the alkyl group followed by the word "alcohol":

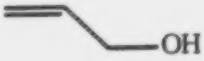
CH_3—OH

methyl alcohol



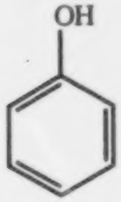
$$\begin{array}{c} CH_3 \\ | \\ CH_3-C-OH \\ | \\ H \end{array}$$

isopropyl alcohol

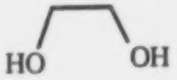


propenol
(allyl alcohol)

Some alcohols just have unique names:

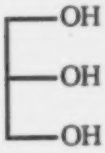


phenol



ethylene glycol

1,2-ethanediol



glycerol

1,2,3-propanetriol

5.2 Hazards of Alcohols

1. Once again, the alcohols are all flammable. They have a much wider flammable range than the hydrocarbons due to their oxygen content.

2. Because they are a little more polar than alkenes and alkynes, they have markedly higher boiling points and their volatility is much lower.

3. Methanol is highly poisonous, can be absorbed through the skin and can lead to blindness. 30 mL has been known to kill a man. Even ethanol from alcoholic beverages can kill in large doses.

4. The lower molecular weight alcohols (C1 - C5) are essentially 100% water soluble.

5. 2-propanol (rubbing alcohol) will poison too, but it is not absorbed through the skin. Ingesting about 100 mL can kill a man.

6. 1,2-ethanediol or *ethylene glycol* (antifreeze) is produced in 2 million ton quantities each year in the U.S., it is quite poisonous and can cause drowsiness, vomiting and renal damage.

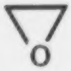
Chapter 6. Ethers

Most ethers are about as inert as alkanes but they can react with air which makes them a special hazard. This functional group is an oxygen -O- in the middle of a chain of carbon atoms. They can also be ring compounds such as the common industrial solvent *tetrahydrofuran*.

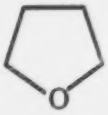
Examples:

$CH_3—CH_2—O—CH_2—CH_3$

diethylether



ethylene oxide



THF

tetrahydrofuran

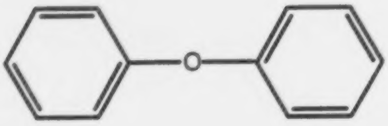
6.1 General Rules for the Nomenclature of Ethers

The guidelines for ethers are too complex, so complex in fact, that many chemists ignore them. Most members of this class have either a unique common name or the following nomenclature is followed.

1. For many simple ethers that are identical on each side of the -O-, just use the prefix *di-* and then the Greek or Latin root word. This is the most convenient naming system.

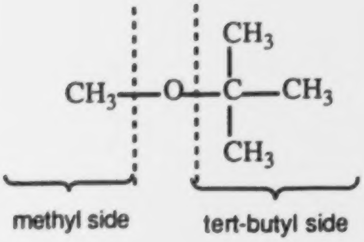
$CH_3CH_2—O—CH_2CH_3$

diethyl ether



diphenyl ether

2. Some ethers have different groups on each side of the oxygen atom. Name these with the smaller alkyl group first then the larger group.

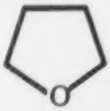


methyl tert-butyl ether

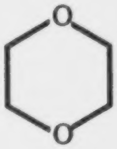
(commonly used in gasoline as an anti-knock compound to replace lead compounds.

6.2 Some Common Ether Solvents

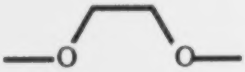
These are used in industry and at universities across the world. They can dissolve many organic compounds.



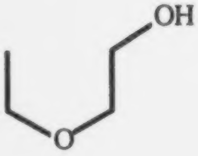
THF



1,4-dioxane

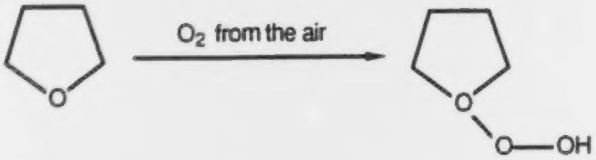


glyme



cellosolve
(ethoxy ethanol)

*******Caution: Ethers Can Form Dangerous Peroxides*******



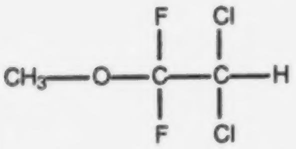
THF

PEROXIDE--EXPLOSIVE

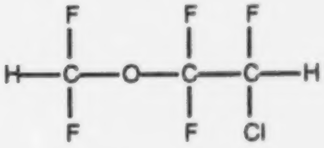
Spotlight—Ethers as an Anesthetic

One of the earliest uses for ethers was as an anesthetic. William Morton, a dentist, first used diethyl ether in 1846 and introduced the medical community to "painless" surgery and dentistry. This chemical invention, along with chloroform, revolutionized the medical profession and established the used of general anesthetics.

In small amounts diethyl ether and other ethers cause a desensitization to pain called *analgesia*. In larger doses, diethyl ether causes unconsciousness and complete muscle relaxation. The ether dissolves into a nerve cell and blocks the transmission of nerve impulses. After surgery, ethers are easily and rapidly expelled from the body by dissolving out to the cells. Due to their extreme flammability and several fire deaths (actually during surgery from instrument sparks or static electricity), diethylether was abandoned as a general anesthetic. By 1985 new anesthetics were in use but these require greater care in administration since the effective dose may be 40–60% of the lethal dose! These include the trade name compounds Penthrane and Enthrane. The addition of the halogen atoms removes the flammability hazard.



Penthrane



Enthrane

6.3 Hazards with Ethers

1. All are flammable, have a wider flammable range than hydrocarbons, and are generally quite volatile.

2. Ethylene oxide is an acute inhalation hazard and can rapidly cause skin irritations and tissue damage.

3. Diethyl ether produces unconsciousness by depressing CNS activity.

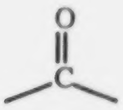
4. Many ethers are explosive when mixed with air.

5. Most ethers (uninhibited) form explosive peroxides upon sitting and have caused plant explosions.

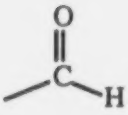
Chapter 7. An Introduction to the Carbonyl Functional Group

There are a plethora of these functional groups in chemistry. The basic group is a carbon with a double bond to an oxygen: C=O. Small changes in the arrangements of atoms around the carbonyl group impart a marked change to the physical and chemical properties of these compounds.

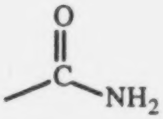
Examples:



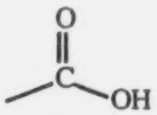
a ketone



an aldehyde



an amide

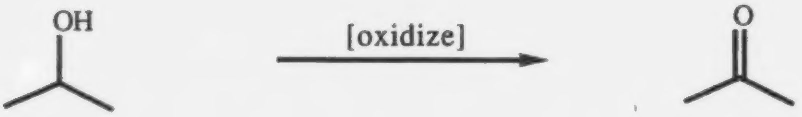


a carboxylic acid

7.1 Oxidation States and Unsaturation

When an organic compound becomes oxidized, usually a loss of hydrogen atoms occurs and/or more oxygens are added to the molecule. The carbonyl has two states of oxidation above the alcohol.

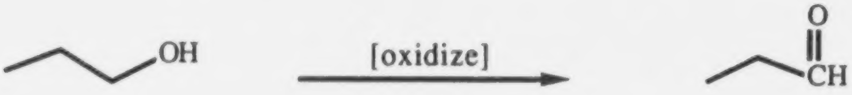
When the alcohol is in the middle of a chain, only one oxidation can occur:



alcohol

ketone
(cannot oxidize further)

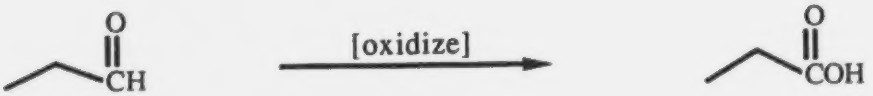
When the alcohol is at the end of a chain, there are two levels of oxidation available. The first level is an aldehyde:



alcohol

aldehyde

The second level is a carboxylic acid with much different properties:

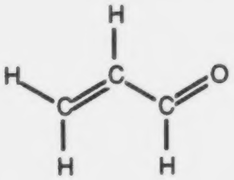


aldehyde

carboxylic acid

Spotlight—Acrolein

Notice that the molecule acrolein contains both an alkene and an aldehyde. Acrolein is a volatile, colorless organic compound with an acrid smell. In very dilute concentrations it smells like an outdoor barbecue and it contributes considerably to the pleasant aroma. Acrolein is easily detected in smoke.



acrolein

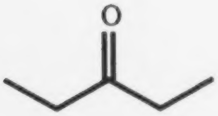
Because acrolein is a component of smoke, it can be highly irritating. This compound is used extensively in the polymer industry as a monomer (starting material). It is extremely flammable with a flash point of less than 0°C and it boils around 95°C. It is also quite toxic and is considered lethal above a concentration of 10 ppm for a short period of time. It is thought to be "unbearable" for brief moments at 24 ppm.

Chapter 8. Ketones and Aldehydes

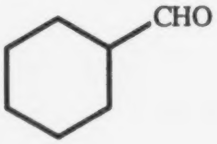
Aldehydes contain the -CHO functional group and must be at the end of an alkyl chain. The simplest member of this class is formaldehyde. It is a gas when pure but it is easily dissolved in water to form a solution known as *formalin*. It causes a burning sensation on the nose and respiratory tract which you may remember from high school. (Because formaldehyde is an alkene, it can polymerize. To prevent this, formaldehyde solutions typically contain 15% methonal.) It is also a component of wood smoke (burns the eyes) and is used as a dried meat preservative.

Ketones contain a carbonyl flanked by two alkyl groups. It must occur in the middle of a chain. These compounds are found in auto shops where they soak grease off auto parts. Thus a common use for these materials is as solvents and as polymer precursors. Acetone, MEK, and MIBK and other ketones are common constituents of paints, varnishes, and resins.

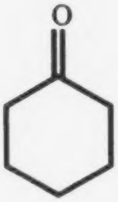
Examples:



diethyl ketone



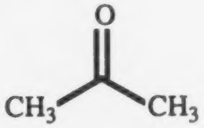
cyclohexanecarboxaldehyde



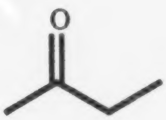
cyclohexanone

8.1 General Rules of Nomenclature for Ketones and Aldehydes

Common names for ketones use the word ketone at the end of the name preceded by the two groups on each side of the carbonyl similar to what we saw in the ether family.

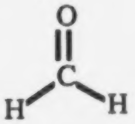


2-propanone
(acetone)



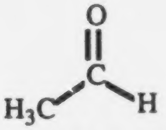
2-butanone
(methyl ethyl ketone)

Besides acrolein, there are only a few common name aldehydes I know of:



(methanal)

formaldehyde

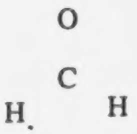


(ethanal)

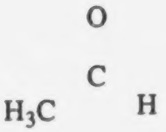
acetaldehyde

IUPAC names for aldehydes are much more common. Use these rules:

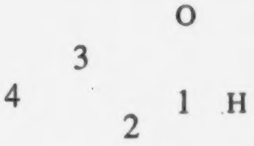
1. Find the longest chain that contains the aldehyde, number the carbonyl as #1. The position of the carbonyl does not have to be stated in the name, it is always understood to be one.



methanal

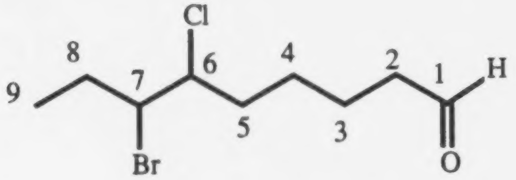


ethanal



butanal

2. Use the root word shown in the Table and follow it with "al":

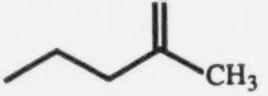


7-bromo-6-chlorononanal

3. Sometimes we use carboxaldehyde for cyclic structures. Remember, the aldehyde must always be at the end of a chain or the compound is a ketone.

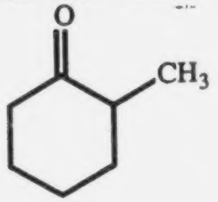
The IUPAC names for ketones are also fairly easy, so use these rules:

1. Use the alkanone to describe a ketone by dropping the "e" on the alkane root word and adding "one." Put the ketone nearest the end of the chain:

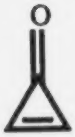


2-pentanone

2. Cyclic molecules use the prefix "cyclo" as we learned earlier:

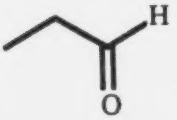


2-methylcyclohexanone

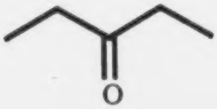


cyclopropanone

4. There are several ways to write ketones and aldehydes:



≡ CH_3CH_2CHO ← not an alcohol



≡ $CH_3CH_2COCH_2CH_3$ ← not an ether

8.2 Hazards with Ketones and Aldehydes

1. These are all flammable compounds.

2. Acetaldehyde is a narcotic and can cause respiratory paralysis.

3. Formaldehyde is a gas which is highly irritating to the mucous membranes.

4. Acetone can cause bronchial irritation and narcosis in large amounts.

5. Toxicity is much more pronounced in the aldehyde rather than the ketone family.

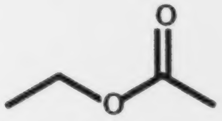
Chapter 9. Carboxylic acids, Esters and Amides

Carboxylic acids contain the -COOH group. The simplest member of this class is formic acid, which can come from red ant bites. The next member is acetic acid, a common constituent of vinegar (5% in water). These are weak acids, but perhaps as strong as an organic acid usually gets, hence the name *acids*. We will discuss acids in greater detail when we deal with corrosives in a later chapter.

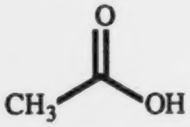
A close cousin of the carboxylic acid is the ester. The flavor industry produces tons of esters each year which we eat and drink in soda pop, candy, desserts and other foods. In addition esters are found in many fragrances and perfumes. They are also used as synthetic oils in many automobiles and airplanes. This functional group is a -COO- with an alkyl group on either end. It is interesting to note that the word "ester" is never used to name a compound except for the generic term "polyester".

Amides are a functional group found frequently in biological systems like proteins and in amino acids. Such bonds are sensitive to bases. It consists of an arrangement of atoms like this: $-CONR_2$. The insect repellant industry makes tons of amides each year because these are the most effective materials to use.

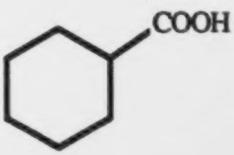
Examples:



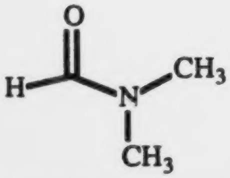
ethyl acetate



acetic acid



cyclohexanecarboxaldehyde

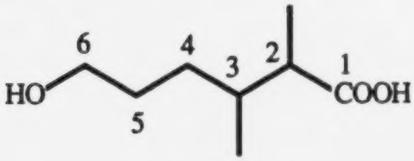


N,N-dimethylformamide

9.1 General Rules for the Nomenclature of Carboxylic Acids

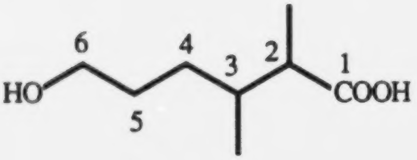
The carboxylic acid functionality is always at the end of a chain. It looks like this: -COOH. For IUPAC names, use the following guidelines:

1. Replace the "e" ending from the Table with "oic" and as before the longest chain should have the acid functional group at the #1 position on the chain.

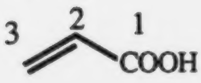


a hexanoic acid

2. The -COOH has the highest priority of any functionality studied so far, because it is the most oxidized.

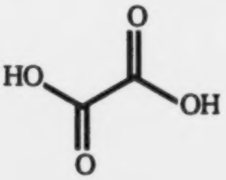


full name:
2,3-dimethyl-6-hydroxyhexanoic acid

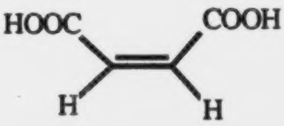


another example:
propenoic acid

3. Some carboxylic acids appear twice in a molecule, these are called 'dioic" acids or commonly named diacids:

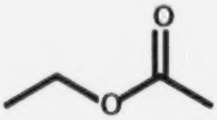


ethanedioic acid



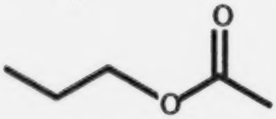
cis-2-butendioic acid

9.2 Some Common Esters—The Acetates

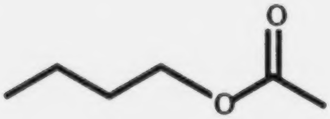


ethyl acetate

used in fingernail polish

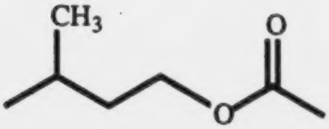


propyl acetate



butyl acetate

common paint solvent and plasticizer



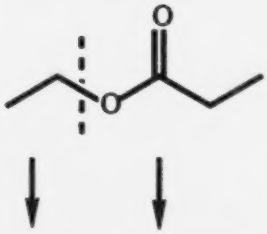
iso-amyl acetate
(banana oil)

used for fit-testing respirators

9.3 General Rules for the Nomenclature of Esters

The ester unit is a combination of a carboxylic acid and an alcohol. It has a -COO- in the middle of the chain of carbon atoms. These are named by IUPAC as follows:

1. **Name the ester as an alkyl alkanoate.**

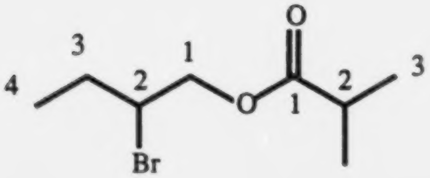


ethyl propanoate

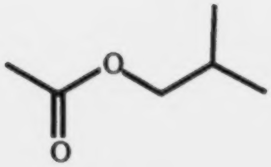
the part on this side of the ester is the alkyl

the part on this side of the ester is the alkanoate

Some other examples are:



2-bromobutyl-2-methyl propanoate



isobutyl propanoate

component of rum

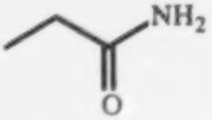
Spotlight—Acetic Acid and Sourdough Bread

A colorless liquid with a sharp aroma, acetic acid is produced in multi-ton quantities in the United States each year. It is the principal acid component of vinegar, a word derived from the French *vin aigre*, meaning sour wine. Vinegar is an oxidized form of the ethyl alcohol in wine and it forms when the cork is left off the bottle for a long period. Acetic acid is also produced in the dough- leavening yeast, *Saccharomyces exiguus*. Another yeast, *Lactobacillus sanfrancisco*, excretes large amounts of acetic acid and lactic acid when dough is raised. These doughs were first prepared regionally in San Franscisco and gave a slight sour taste to their breads when baked. Today we can buy these breads everywhere; they are simply called sourdough bread.

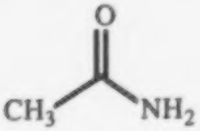
9.4 General Rules for the Nomenclature of Amides

The IUPAC names for amides are:

1. Replace the "e" ending with "amide"

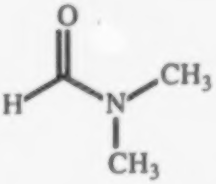


propanamide



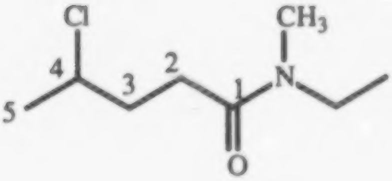
ethanamide
common name: acetamide

2. The groups on the nitrogen are preceded by N- or N,N-



N,N-dimethylformamide

common name: dimethylformamide (DMF)



4-chloro-N-ethyl-N-methylpentamide

9.5 Hazards of Carboxylic Acid Groups

1. The vapor of dimethylformamide is very harmful. 100 ppm can cause liver injury. It can pass through the skin and carry any other chemicals with it.

2. Ethamide and a number of other amides are irritants.

3. Formic acid is dangerously caustic to the skin.

4. Acetic acid can also burn the skin and cause vomiting, diarrhea, collapse of the circulatory system, even death when used in concentrated form.

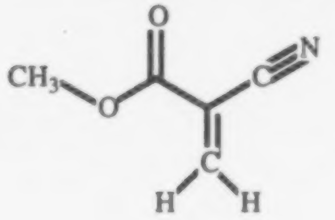
5. Most other carboxylic acids are poisonous.

6. Most esters are irritants when concentrated vapors are inhaled.

Spotlight—Methyl Cyanoacrylate--*Super Glue*

The structure of methyl cyanoacrylate contains an alkene, a nitrile or cyano group and an ester. When spread on the surfaces of two things to be joined, it starts to form polymers, like plastics and synthetic rubber. This happens because surfaces often contain traces of alcohols and water which start the polymerization chain reaction.

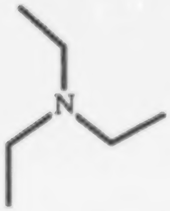
Unfortunately, Super Glue can also stick to your fingers and can actually bond things to your skin. Surgeons have known this for a long time because it can be used in place of sutures. The structure of methyl cyanoacrylate is shown below.



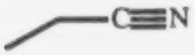
Chapter 10. Nitriles and Amines

Both of these groups contain nitrogen in two different ways. The nitrile functionality is a -CN group on the end of a chain. It contains a triple bond. An amine contains a nitrogen at any part of the chain. The nitrogen can bear alkyls or hydrogens.

Examples:



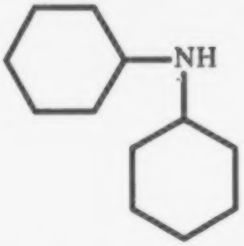
triethylamine



propanenitrile

CH_3NH_2

methylamine



N,N-dicyclohexylamine

10.1 General Rules for the Nomenclature of Nitriles

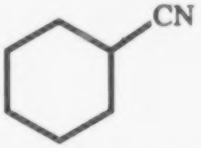
The IUPAC systematic nomenclature for nitriles uses:

1. Use "nitrile" on the ending of the name without removing the "e" on the alkane root word.

CH_3CN

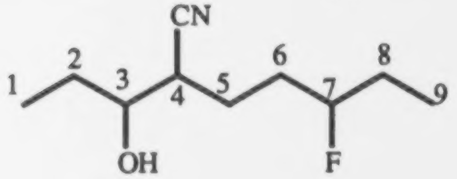
ethanenitrile

common name: acetonitrile



cyclohexanenitrile

2. Sometimes we use of the term "cyano" to name -CN as a functional group in long chain and off of rings.

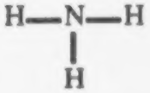


4-cyano-7-fluoro-3-nonanol

Common names are not used often except for ethanamide or acetonitrile (methyl cyanide); this is a very polar solvent which can pass directly through the skin. (structure is above)

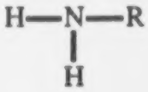
10.2 General Rules for the Nomenclature of Amines

Amines come is three varieties, depending on the substitution on the nitrogen. Ammonia is the parent molecule, however, it is not an organic molecule because it contains no carbon.



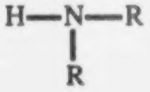
$H-\underset{H}{\underset{|}{N}}-H$

ammonia



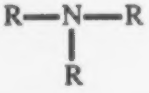
$H-\underset{H}{\underset{|}{N}}-R$

primary amine



$H-\underset{R}{\underset{|}{N}}-R$

secondary amine

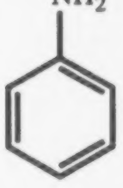


$R-\underset{R}{\underset{|}{N}}-R$

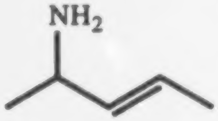
tertiary amine

These are named as alkanamines by IUPAC nomenclature:

1. This time we replace the "e" ending on the Table with "amine." For primary amines, we call them simple amines:

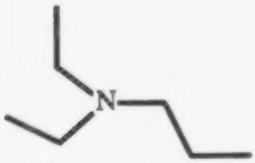


benzenamine



trans-3-penten-2-amine

2. For secondary and tertiary amines, we use an N- for each substituent or an N,N- for disubstituted amines.

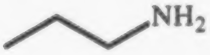


N,N-diethylpropanamine

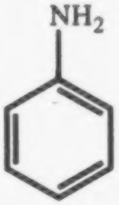
common name:
N,N-diethylamino propane

$CH_3NHCH_2CH_3$ N-methylethanamide

3. An alternative way to name amines is to use "amino" to designate the structure.



aminopropane



aminobenzene

Notice that aminobenzene and benzenamine were both used to describe the ring structure. By far the most common way to designate these molecules is by the common name, **aniline**. These are derivatives of the aromatic compound benzene which is discussed in the following chapter.

10.3 Some Hazards of Nitriles and Amines

1. Many amines are physiologically active and are found in nature as alkaloids. These chemicals are potent central nervous system stimulants and can increase blood pressure and raise body temperature. Some of these are mescaline, THC, and hundreds of life-saving drugs.

2. Acetonitrile can pass through the skin and carry any drug or contaminant chemical into the bloodstream.

3. Most other nitriles, such as propanenitrile and hexanenitrile, are toxic.

4. Many amines are toxic and irritants. Some are human carcinogens.

Chapter 11. Aromatic Compounds

ar·o·mat·ic "of, relating to, or having aroma: *fragrant*" [Webster's New Collegiate Dictionary, 1991] This dictionary definition, logically, should indicate that aromatic hydrocarbons are compounds which have pleasant aromas. Unfortunately, this is rarely the case. While the name is derived from this definition, it does not explain the chemistry of these compounds.

11.1 Benzene

Aromatic hydrocarbons are those compounds which are characterized by the presence of a benzene ring. The parent molecule benzene is a clear, colorless, highly flammable compound with a pleasant odor. Michael Farraday first isolated benzene from coal gas in 1825 but its unique chemical structure baffled scientists for many years until 1865 when a German chemist, August Kekule, proposed the hexagonol structure we now know as the benzene ring. The six carbon atoms in the benzene molecule are arranged as shown in Figure 1 with the carbon atoms bonded together by sharing a pair of electron *(covalence)*. The single bonds between carbon atoms are strong *sigma* bonds. However, the molecular configuration also necessitates the presence of a double bond between alternating carbon atoms. Because of their orbital position, the electrons responsible for this bond are more loosely connected resulting in a weaker *pi* bond. These bonds are less stable than the sigma bonds and are normally associated with increased reactivity. The unique arrangement of the carbon atoms in benzene, however, creates a more stable compound.

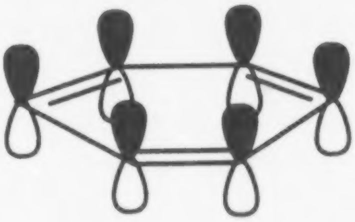
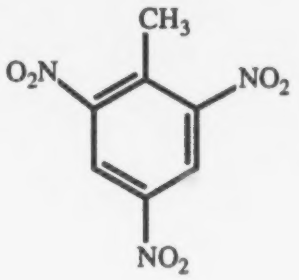


Figure 1. The molecular structure of benzene.

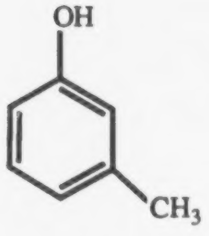
There are several ways to represent the structure of benzene. Chemists draw the molecule without the "dumbbell" lobes shown above and always just assume they are there.

11.2 Arenes

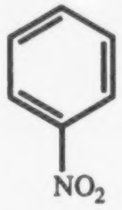
Aromatic hydrocarbons are known generically as *arenes*. This immediately suggests the presence of at least one benzene ring. Three of the simpler arenes are common industrial solvents—benzene, toluene, and xylene. The chemical structures of these compounds are very similar; the only difference being the addition of methyl (—CH_3) groups to the benzene ring. Several examples of these substituted benzenes are shown below.



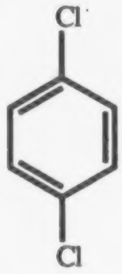
2,4,6-trinitrotoluene
(TNT)



meta-cresol



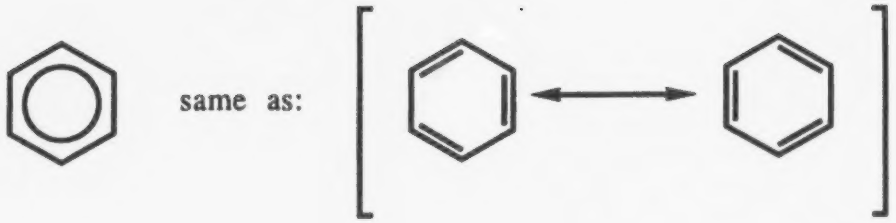
nitrobenzene



para-dichlorobenzene

11.3 Resonance in Aromatic Compounds

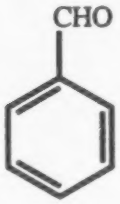
Most aromatic (strong aroma) compounds are derivatives of benzene. It has a reasonably stable structure and is somewhat inert to reactivity. It enjoys a certain stability because of it's conjugated *and* in a ring.



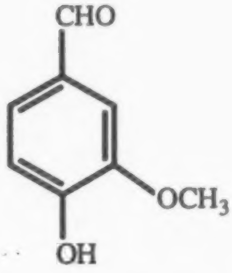
The circle is drawn in the center of the hexagonal structure to show that the electrons that should form a series of alternating double bonds are actually spread among all six carbon atoms, a property known as *resonance*. Many organic compounds which have multiple double bonds exhibit resonance.

11.4 Flavor Aromatics

Unfortunately, many of these compounds were known long before IUPAC such that common names abound. Older German literature suggests that these compounds have been known since the early 1800's. A number of these compounds have profound taste and olfactory responses. Some examples of aromatic compounds from the flavor industry are shown below.



benzaldehyde
(almonds)

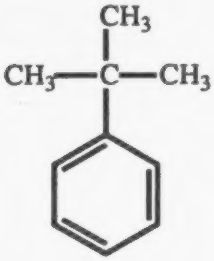


vanillin

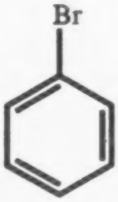
11.5 Nomenclature of Aromatic Compounds

The IUPAC name is still the most acceptable name:

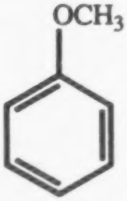
1. For monosubstituted benzenes, the compound is called a benzene:



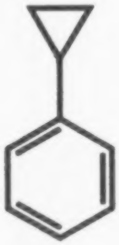
tert-butylbenzene



bromobenzene

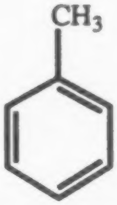


methoxybenzene

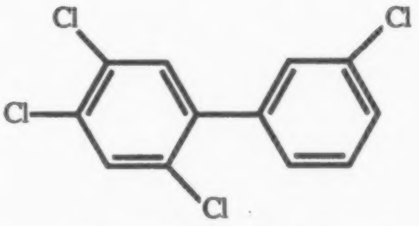


cyclopropylbenzene

2. A less acceptable, but very often used name for aromatic compounds is to use "phenyl" for the benzene.



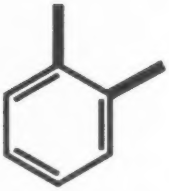
phenyl methane
(toluene)



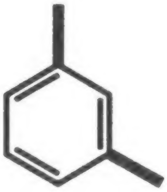
polychlorinated biphenyl

77

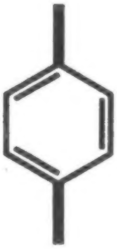
3. For disubstituted benzenes, we use the terms "o-" for ortho, "m-" for meta, and "p-" for para as a prefix in the name:



ortho

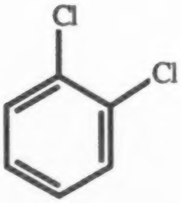


meta

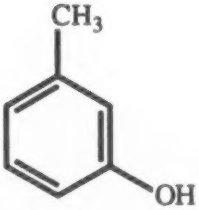


para

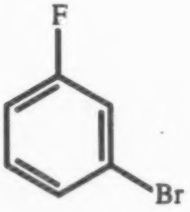
Some examples include:



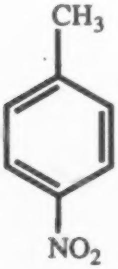
ortho-dichlorobenzene



meta-hydroxytoluene



meta-bromofluorobenzene

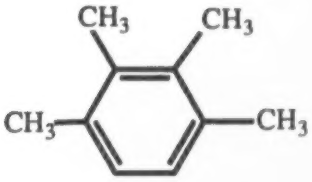


para-nitrotoluene

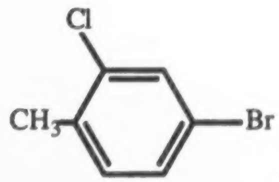
11.6 A Few Comments about Aromatic Isomers

There are three different forms of xylene. All three of these compounds are dimethyl benzene but the second methyl group may be attached to the benzene ring such that three discrete chemical compounds are formed. You recall that these are referred to as *isomers*—compounds which have identical numbers of atoms but different atomic configurations. There are millions of known isomers of organic compounds. In theory, one molecular formula may give rise to billions of isomers. For example, there are 4,111,846,763 possible isomeric forms of squalane, $C_{30}H_{62}$. For practical purposes, commercial grades of xylene contain a mixture of all three isomers, but the meta isomer is the predominant form. Title III Chemical Inventory forms and analytical reports may designate the specific isomer or simply state xylenes meaning all three compounds are present.

4. More highly substituted benzenes use the rules studied earlier:



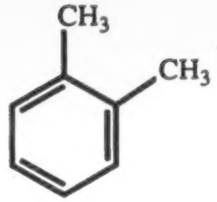
1,2,3,4-tetramethylbenzene



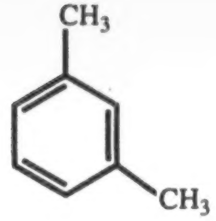
1-bromo-3-chloro-4-methylbenzene

11.7 Common Aromatic Names

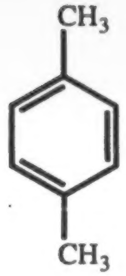
There are many common names for substituted benzenes which you should know. I have had to memorize them. The names are quite old and predate the systematic nomenclature rules. There are several examples shown below. Remember that compounds such as xylenes are often called the generic name "xylenes" for a mixture of all three isomers. Each of the ortho, meta, and para isomers could be present in varying amounts.



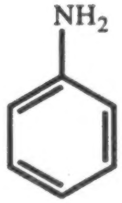
o-xylene



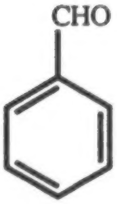
m-xylene



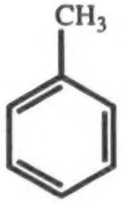
p-xylene



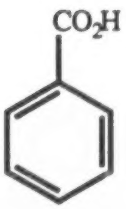
aniline



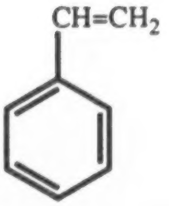
benzaldehyde



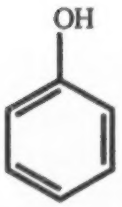
toluene



benzoic acid



styrene

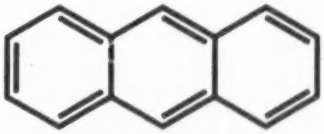


phenol

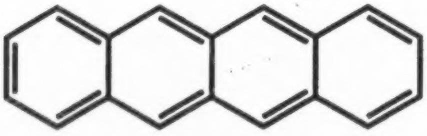
11.8 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic Aromatic Hydrocarbons are *arenes* which consist of three or more benzene rings bonded together. These are especially stable compounds, many of which are known or suspect carcinogens. Figure 3 depicts the chemical structure of four of the most common PAHs. All four are indirectly identified as suspect carcinogens by OSHA as these are components of coke oven emissions. *Coke Oven Emissions* are a complex mixture of coal and coke particles, various vapors, gases, and tars that include PAHs. OSHA defines these emissions as: *"the benzene-soluble* *fraction of total particulate matter present during destructive distillation or carbonization of coal to produce coke"*. [see 29 CFR 1910.1029] PAH's generally account for 2 to 3 percent of the total particulates and 3 to 6 percent of the benzene-soluble fraction. The PEL for these emissions is 150 ug/m^3 on an 8-hour time-weighted average.

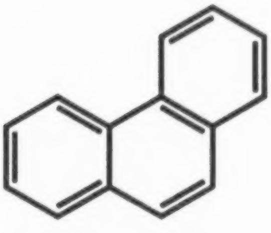
Polycyclic aromatic hydrocarbons, C_{10} and higher, have molecular weights of 178 or greater. [Note: Anthracene ($C_{14}H_{10}$) and Phenanthrene ($C_{14}H_{10}$) are isomers.] They are solids at room temperature and are thus regulated as particulate contaminants. These compounds are all identified as hazardous substances under the Comprehensive Environmental Response, Compensation and Liability Act of 1980 (CERCLA), better known as "Superfund" [see 40 CFR 302.4] and Chrysene (U050) is listed as a hazardous waste under RCRA.



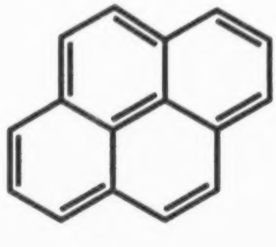
Anthracene



Tetracene



Phenanthrene

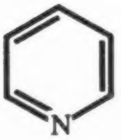


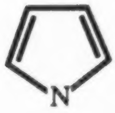
Pyrene

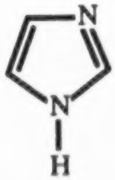
One derivative of pyrene, benzo[a] pyrene, is a definitive cancer-causing agent. Benzo[a] pyrene is a major component of coke oven emissions and cigarette smoke as well as *coal tar pitch volatiles*—another source regulated by OSHA. Cigarette "tar" contains two additional PAH's which are suspect carcinogens, benzo[c] phenanthrene, and benz[a] anthracene. Polycyclic aromatic hydrocarbons, and several other toxic compounds identified in cigarette smoke, increase the risk of contracting lung cancer or emphysema.

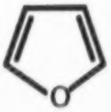
11.9 Heterocycles

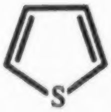
There are many aromatic compounds which contain nitrogen, oxygen or sulfur in the ring. There are many common names in this series as well. Only a few basic rules are given here. A more complete treatment of this subject can be found in other scientific literature. Some simple examples include the following:

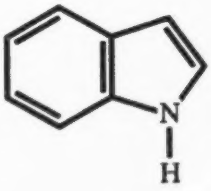

pyridine


pyrrole


imidazole

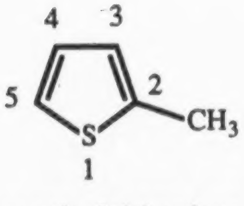

furan

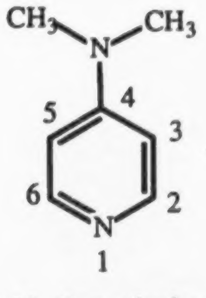

thiophene


indole

For IUPAC systematic nomenclature, we use the following convention.

1. Always number the noncarbon atom as #1, and proceed as before. There is no ortho, para, etc. in these molecules.


2-methylthiophene


4-N,N-dimethylpyridine

11.10 Hazards of Aromatic Compounds

There is sufficient evidence to list benzene as a known human carcinogen. Several case reports as well as epidemiological studies establish a relationship between benzene exposure and leukemia. It is one of 25 substances specifically regulated by OSHA under section 6 (b) of the Occupational Safety & Health Act. [see 29 CFR 1910.1028] The Permissible Exposure Limit (PEL) for benzene is 1 ppm on an 8-hour time-weighted average. While toluene and xylene are both highly flammable, neither has demonstrated carcinogenic effects in humans or in animals.

There is overwhelming scientific evidence from epidemiological surveys as well as animal studies and chemical analyses that supports the finding that coke oven emissions are carcinogenic. Coke oven workers, and people living or working in industrial areas where coke oven emissions occur, have a high potential risk of exposure. Exposed individuals, subsequently, have an increased risk of developing cancer of the lung and urinary tract. In addition, observations on animals and humans have shown that skin tumors can be induced by the products of coal combustion and distillation. To summarize:

1. All of these compounds are flammable and burn with a sooty flame.

2. Benzene itself is probably the most dangerous in this series. It is a known human carcinogen. (leukemia)

3. Phenol is a poisonous compound, however, in small amounts, it is used to treat cold sores. 1 g can kill a man.

4. Toluene (from model glue) can be narcotic at high concentrations. As little as 1 percent by volume in air can be immediately fatal.

5. A large number of the aromatic compounds can be irritants and damage the mucous membranes.

6. Because of the large number of compounds in this series, consult a Merck index, material safety data sheet (MSDS), or chemical dictionary for toxicity and health data on a specific compound.

Spotlight—Polychlorinated Biphenyls (PCBs): A Perspective in Toxicity

Probably no single chemical compound is better known than PCB's. The press has literally bombarded the public with stories relating the incidences of spills, leaks, and exposures to these materials. But what exactly are PCBs, and how hazardous are they?

PCB is an abbreviation for *polychlorinated biphenyl* . The structure of this compound is relatively simple consisting of two benzene rings connected together with a covalent bond between two carbon atoms. Polychlorinated biphenyls are sometimes referred to as *Chlorodiphenyls*, a term NIOSH prefers.

The term **polychlorinated** means there are many chlorine atoms attached to the compound. [poly = Greek for many] There are ten carbon atoms on each biphenyl available for bonding. Two or more chlorine atoms may be attached to the diphenyl ring such that 209 different structures or *isomers* may be formed. The physical,chemical, and toxicological properties of these compounds vary but all forms are stable at elevated temperatures and are insoluble in water. The appearance may vary from an oily liquid to a white crystalline solid to a hard, noncrystalline resin. The physical and chemical characteristics made PCB's an excellent choice for use as in transformers, capacitors, hydraulic fluids, printing inks, carbonless copy paper, paints, caulking compounds, and sealants. Three (3) major forms of PCB's representing 72 different structures have been widely used. These are summarized in Table 5.

Monsanto first introduced PCB fluids in 1929. Before the United States banned the manufacture of PCB's in 1979, Monsanto had produced well over *one billion pounds* of PCB's. Ninety-five percent (95%) of all capacitors [approximately 100 million] manufactured prior to 1979 used PCB fluids. Monsanto gave PCB's the trade name **Aroclor**. Most transformer fluids are mixtures of an Aroclor and a thinning solvent such as trichlorobenzene. The most commercially important are Aroclor 1242, Aroclor 1254, and Aroclor 1260. The last two digits denote the percentage of chlorine atoms.

Arochlor	MW	% Chlorine	No. of Cl atoms
1242	257.5	41.3	three
1254	326.5	54.4	five
1260	351.0	60.7	six

Table 5. Aroclor Summary

PCB Toxicity

The same heat resistance properties that make PCB's a desirable material for use in transformers, capacitors, etc. result in environmental stability of these compounds. Their biological persistence allows transport through the food chain resulting in increased doses to animals higher up the chain. Toxic effects in animals have been noted such as liver tumors in rats; thinning in bird eggshells; lower egg production; and deformity at birth. Certain acute and chronic toxic effects have been noted in humans although the evidence for carcinogenicity is inadequate. The most common symptoms of severe exposure are: contact dermatitis, Chloracne (a darkening or pigmentation of the skin), skin rashes, itching, eye irritation, dry throat, nausea, dizziness, headaches. An incident in Yusho, Japan in 1969 exposed thousands of people to PCB's when rice bran oil used in cooking was contaminated by heat transfer fluid leaking from a broken pipe. The unsuspecting Japanese actually *ingested* large doses of PCB's. To my knowledge no deaths occurred from this exposure. Many people experienced the symptoms identified above as well as some cases of liver damage.

Since the toxic effects of PCB exposure are relatively minor compared with such compounds as Arsenic, Cyanide, Phosgene, Trichloroethylene, Methyl Isocyanate, or Formaldehyde, why the concern? Why did Congress pass the Toxic Substances and Control Act (TSCA) in October, 1976, a portion [Section 6 (e)] of which deal specifically with the production, use, storage, and disposal of PCB's? Why the newspaper accounts espousing the hazards of PCB's?

Several reasons. First, as stated earlier, since production began in 1929, well over 1 billion pounds of PCB's have been manufactured. The release of PCB's into the environment from prior industrial uses went largely unchecked until 1979. Second, PCB's are essentially resistant to biological degradation. Third, bioaccumulation of PCB's in the *adipose* or fatty tissues through ingestion of contaminated foods. Fourth and most significant, the formation of toxic by-products during manufacture or incomplete combustion of PCB's. Two species of special interest: chlorinated dibenzofurans and dioxins. The basic chemical structure of these is shown on the first page of this book. One particular isomeric form of dioxin, 2,3,7,8-Tetrachlorodibenzodioxin, was responsible for the relocation of the entire community of Times Beach, MO when elevated levels were found in the soil. There is some disagreement among toxicologists as to the adverse effects of these compounds on man but they appear to demonstrate chronic effects at very low concentration.

PCBs In Food

Due to the widespread use of PCB's in industry, their biological stability, the accumulation in the food chain, and the volume produced, PCB's have been identified in soaps, ceiling tile, paints, and paper food packaging materials, PCB's have become the most ubiquitous of all contaminants. Tissue assays of over 4000 samples in the 1970's suggest that the entire U.S. population is carrying some body burden of PCB's. Even the Food and Drug Administration (FDA) has gotten involved. In 1973, FDA first established tolerances for PCB's in certain foods, in 1979, four of those tolerances were lowered. The tolerances are now **1.5 ppm** (fat basis) in milk and manufactured dairy products, **3 ppm** (fat basis) in poultry, **0.3 ppm** in eggs, **0.2 ppm** in finished animal feed, **2 ppm** in animal feed components of animal origin, 2 ppm in fish and shellfish (edible portion), and **0.2 ppm** in infant and junior foods. FDA has established action levels of **3 ppm** (fat basis) in red meat and **10 ppm** in paper food-packaging material.

PCB Exposure Limits

OSHA has established a Permissible Exposure Level of 1 mg/m^3 for Aroclor 1242, and a PEL of 0.5 mg/m^3 for Aroclor 1254 and 1260. The PEL expressed in ppm for Aroclor 1242, and Aroclor 1254 respectively are 0.095 and 0.037. NIOSH however, recommends an exposure level of only 1 ug/m^3. The NIOSH exposure level for Aroclor 1254 expressed in ppm, is 0.000075!

85

Chapter 12. Flammable Materials

12.1 Basic Elements for Combustion

Combustibility is the ability of a material to act as a fuel. Materials that can be readily ignited and continue burning are considered combustible. Three elements are essential for combustion:

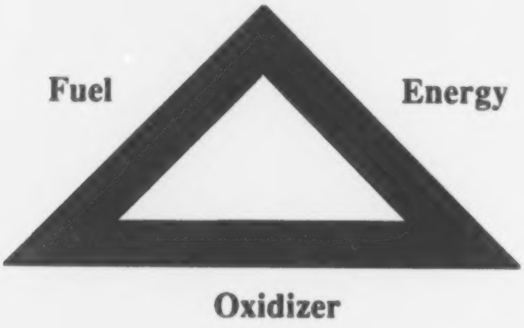
1. fuel;
2. oxygen or an oxidizing agent;
3. heat or energy

The mixing ratio of fuel:oxygen must be within a certain range to ignite and maintain the burning process. Combustion is a **chemical** reaction which requires heat to proceed:

$$\textbf{fuel} + \textbf{oxygen} \xrightarrow{\textit{heat}} \textbf{products}$$

Heat is either supplied by the ignition source and maintained by the combustion, or supplied from an external source. The relationship of the three components enumerated above is best illustrated by the fire triangle; a concept that has been understood for centuries.

Figure 1. The Fire Triangle



Most fires can be extinguished by eliminating one of these components. For example, water applied to a Class A fire removes the heat, thereby extinguishing the fire. When a material itself generates sufficient heat to self-ignite, (autoignition temperature) spontaneous combustion occurs,

occurs resulting in a fire or explosion. Another fire theory recognizes a fourth leg to this simple diagram—*the chain reaction of burning*. This concept involves the formation of *free radicals* during the combustion process. These free radicals are formed when a carbon-carbon bond breaks leaving an unpaired electron attached to part of the original molecule. These highly-reactive free radicals intensify combustion by breaking additional carbon-carbon bonds which releases enormous amounts of energy.

12.2 Classes of Fire

Class **A** (**A**sh)	A fire involving ordinary combustible materials such as wood, paper, cloth, and some rubber and plastic materials.
Class **B** (**B**oils)	A fire involving flammable or combustible liquids, flammable gases, greases and similar materials, and some rubber and plastic materials.
Class **C** (**C**onducts)	A fire involving energized electrical equipment where safety to the employee requires the use of electrically nonconductive extinguishing media.
Class **D** (**D**ents)	A fire involving combustible metals such as titanium, magnesium, zirconium, sodium, potassium, lithium.

12.3 Halon Extinguishers

"Halon" is a generic term derived from the word "halogen" which refers to the elements found in Group VII A of the Periodic Table, specifically, Flourine, Chlorine, Bromine, and Iodine. The fire-fighting properties of these elements in a hydrocarbon base have been noted since the 1940's. However, the realization that these compounds were physiologically toxic to varying degrees has minimized or eliminated their use. Carbon tetrachloride (CCl_4), for instance, is outlawed as a fire extinguishing agent in government installations. Only two Halon extinguishing agents are widely used today: bromochlorodifluoromethane (CF_2ClBr)—Halon 1211; and bromotrifluoromethane (CF_3Br)—Halon 1301.

These numbers represent a unique nomenclature system to classify the Halon agents. A series of three or four digits designates the number of carbon and halogen atoms in the compound as shown below:

first digit: number of carbon atoms
second digit: number of fluorine atoms
third digit: number of chlorine atoms
fourth digit: number of bromine atoms

For example carbon tetrachloride was known as Halon 104, indicating its chemical structure as CCl_4.

Because these extinguishing agents are "clean", that is they generally leave only a minor residue following their application to a fire, they are ideally suited for the protection of delicate electronic equipment, computer circuits, aircraft interiors, museums, hospitals, and many other areas. Halon extinguishers are normally very effective for Class A, B, or C fires.

However, there are several disadvantages: Halon agents may not be used on Class D fires. All are somewhat toxic. In extreme fire conditions, halon agents will decompose generating toxic combustion products such as hydrogen fluoride, hydrogen chloride, phosgene, and other gases. Most importantly, these substances have the highest Ozone Depletion Factors (ODF) of any compound as noted in the 1990 Clean Air Act Amendments.

Nonetheless, Halon extinguishers may still be the best choice for certain specific applications and will continue to be widely used where other materials are either ineffective or impractical or until substitutes are developed.

12.4 Flammable Solids

In order to adequately define flammability one must differentiate between the physical state of the materials in question. The Department of Transportation (DOT) has established three distinct classifications for flammable materials based on physical state -- **solid, liquid, or gas.** While flammable solid materials represent an extreme hazard due to their reactivity or extremely hot flame, our study of hazardous materials chemistry will be limited to very few of these substances.

DOT defines a **Flammable Solid** as:

> Any solid material, other than an explosive, which, under conditions normally incident to transportation is liable to cause fires through friction, retained heat from manufacturing or processing, or which, can be ignited readily and when ignited burns so vigorously and persistently as to create a serious transportation hazard. Included in this class are spontaneously combustible and water-reactive materials

12.5 Flammable Liquids

The use of the term **Flammable Liquid** is somewhat misleading in that liquids **do not burn.** Liquids produce vapors through evaporation or volatilization and it is these vapors in combination with air (oxygen actually), that sustain combustion. The relative flammability of a liquid is determined by its **flash point**—which is defined as *the minimum temperature of the liquid at which a spark or flame can cause an instantaneous flash in the vapor space above the liquid.* Flash points for some common flammable liquids are listed below:

gasoline	-45°F	-43°C
acetone	0°F	-18°C
benzene	12°F	-11°C
diesel fuel	125°F	53°C

The flash point of a liquid is determined by one of two types of testing chambers: Open Cup or Closed Cup. The testing apparatus consists of a small chamber in which the sample is placed, a thermometer or thermocouple to measure temperature, and an open flame which is passed over the sample as a source of ignition. The sample is slowly heated until a "flash" occurs. The temperature of the liquid where this occurs is the flash point.

DOT regulations specify that any substance having a flash point below 100°F is classified as a flammable liquid while substances having a flash point between 100°F—200°F are classified as combustible liquids. OSHA uses flash point and boiling point to differentiate three types of flammable liquids, and flash point only to differentiate three types of combustible liquids. See Table 6.

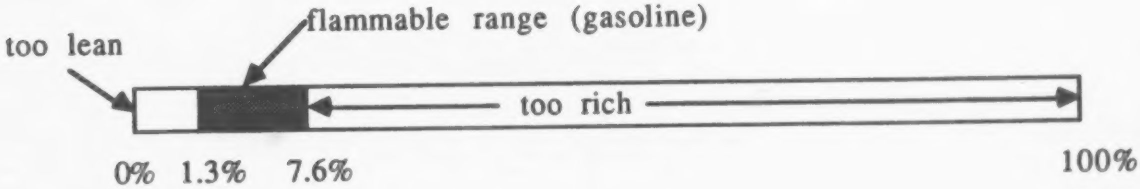
EPA regulates liquid wastes for the hazard characteristic of **ignitability** if the flash point is less than 140°F pursuant to 40 CFR Part 261. EPA has designated the specific alpha-numeric code of **D001** for these wastes. Flammable solids, oxidizers, and flammable gases are also classified hazardous in this category. Flammable gases are classified by DOT as either a mixture of 13 percent or less by volume with air which forms a flammable mixture, or the flammable range with air is wider than 12 percent, regardless of the lower limit.

Flammable Liquids-OSHA		**Flammable Liquids-DOT**	
IA	flash point < 73°F boiling point < 100°F	PG I	flash point N/A initial boiling point ≤35°C (95°F)
IB	flash point < 73°F boiling point > 100°F	PG II	flash point <23°C (73°F) boiling point >35°C
IC	flash point < 100°F	PG III	flash point ≥23°C, ≤60.5°C (141°F) boiling point >35°C
Combustible Liquids-OSHA		**Combustible Liquids-DOT**	
I	flash point 100-139°F	flash point >60.5°C, <93°C (200°F)	
IIIA	flash point 140-199°F	N/A	
IIB	flash point > 200°F	N/A	

Table 6. OSHA/DOT Classes of Flammable and Combustible Liquids

12.6 Lower Explosive Limit and Upper Explosive Limit

There are two other properties of flammable materials that of which the Non-Chemist should at least be aware: *Flammable range, and autoignition temperature*. The flammable range is simply the difference between the **upper explosive limit** (UEL) and the **lower explosive limit** (LEL).



UEL is defined as the **maximum** volume percent of a material (gas of vapor) in air at which ignition can occur; while the LEL is the **minimum** volume percent of a material (gas or vapor) in air at which ignition can occur. Examples are listed below:

gasoline	LEL=1.3%	UEL= 7.6%	FR = 6.3%
ethyl ether	LEL=1.9%	UEL=36.0%	FR = 34.1%
carbon disulfide	LEL=1.3%	UEL=50.0%	FR = 38.7%
hydrogen	LEL=4.0%	UEL=75.0%	FR = 71.0%

The best analogy is a gasoline engine. During normal operation, gasoline is vaporized through the carburetor venturi into the cylinders where combustion occurs. This process will repeat itself several thousand times a minute as long as the gasoline vapor:air mixture is within the flammable range, i.e. between 1.4%—7.6%. If an insufficient amount of gasoline is vaporized, the mixture is too lean, i.e. below the LEL, and combustion cannot occur. When an engine is "flooded", the upper explosive limit has been exceeded and the mixture is **too rich** to burn.

12.7 Autoignition Temperature

The autoignition temperature is the minimum temperature at which rapid combustion becomes independent of external heat sources. That is once a material has reached its autoignition temperature, it will spontaneously combust in the absence of additional external heat. Ray Bradbury once wrote a book entitled **Farenheit 451,** referring to the autoignition temperature of paper.

gasoline	536°F
carbon disulfide	194°F
isopropyl alcohol	750°F

Some substances have extremely low autoignition temperatures as shown in the examples listed above.

Chapter 13. Physical/Chemical Properties

13.1 Solubility

The ability of a solid, liquid, gas, or vapor to dissolve in water is its solubility. An insoluble substance can be mixed or blended in water for a short time but will tend to maintain its own integrity as a solid, liquid, or gas and will coalesce or group together. The solubility of a substance is independent of its density or specific gravity. Simply put, it is the degree to which a substance is capable of mixing with water with no observable phase separation. Materials which readily dissolve are said to be **miscible**, while materials that do not dissolve are said to be **immiscible**. Water is referred to as a universal solvent—one that will dissolve everything. At face value this does not appear to be the case since we cannot see oil dissolving in water for instance. However, to varying degrees, everything does dissolve in water even if the amount if but a few parts per million.

13.2 Density/Specific Gravity

The density of a substance is its mass per unit volume, usually measured in grams per cubic centimeter (**g/cc**). However density can be stated in other terms using the Avoirdupois system. For instance, pounds per gallon (**lbs/gal**), and tons per cubic yard (**tons/yd^3**). The density of water is 1.0 g/cc at 4^{o}C since one cc of water at this temperature has a mass of one gram. If the density of substance **A** is **x** g/cc then the specific gravity is expressed as:

$$\boxed{A = \frac{\mathbf{x}\text{ g/cc}}{1.0\text{ g/cc}}} \text{ or simply } \underline{\mathbf{x}}$$

Specific gravity is a relative measurement based on the density of a substance divided by the density of water, which is 1.0 g/cc at 4^{o}C. Water is one of the few very unique materials that actually increases in volume as it solidifies. If a given substance is insoluble and the specific gravity is greater than one, the substance will sink; if the material is insoluble and the specific gravity is less than one, the material will float. This is an important property when considering mitigation and treatment methodologies.

13.3 Freezing point/Melting point

When discussing various temperatures of substances which define certain physical properties, scientists use the word point. For example the freezing point is the temperature at which a liquid solidifies. This can be better understood if we think in terms of the molecules which comprise any given substance. In a gas, the molecules are the farthest apart and moving the most rapidly. If confined a these gas molecules will exert pressure on the sides of the container. The more gas molecules one places into the container, the greater the resulting pressure. When cooled and/or pressurized, a gas will convert into a liquid. When this occurs, the molecules coalesce and their motion decreases. Liquids assume the shape of their container. Continued cooling and/or pressurization will solidify the liquid. At this temperature (the **freezing point**), molecules are closely packed and molecular motion slows to its lowest speed. When this now solid material is converted back into a liquid (the **melting point**), the molecules again separate and molecular motion increases. Please observe that the melting point and freezing point of a substance is the same temperature. We use the different points to indicate from which state we are converting. For example water (as a liquid) freezes at 32^{o}F. Water as a solid (ice) melts as 32^{o}F. These temperatures are useful to describe the most common physical state of a substance.

13.4 Vapor Pressure

A liquid in a closed container at a given temperature will evaporate into the space above the liquid until **equilibrium** is reached between the liquid and its vapor. Equilibrium is characterized by two opposing changes which occur simultaneously. In our closed container, some of the liquid evaporates while some of its vapors condense back into the liquid phase. The pressure exerted by the liquid at equilibrium, is the vapor pressure of the liquid at that temperature. It is a measure of the liquid's ability to vaporize or evaporate. Normally, the MSDS reports the vapor pressure at 68^{o}F.

Vapor pressure is a physical property characteristic of all liquids, and some solids, and varies with temperature. As the temperature increases, more and more of the liquid or solid vaporizes, and the pressure correspondingly increases. Vapor pressure curves for all liquids are similar. A liquid which will vaporize readily at relatively low temperatures is said to be **volatile**. Solids can also vaporize. **Dry ice** (solid carbon dioxide) has a very high vapor pressure although it is a solid material. The ability of a solid to go directly from the solid to the vapor state is called **sublimation**.

The Department of Transportation (DOT) defines liquids and gases based on vapor pressure. A gas is defined as having a vapor pressure exceeding 40 psia (absolute—meaning atmospheric pressure (14.7 psi) is included in the measurement. Liquids are defined as having a vapor pressure less than or equal to 40 psia. However, vapor pressure is usually measured using a manometer (a U-shaped tube filled with mercury) which is typically calibrated in millimeters. Atmospheric pressure is measured in either inches or millimeters of mercury (Hg), or in pounds per square inch (psi).

13.5 Evaporation Rate

By dividing the vapor pressure of a liquid by the vapor pressure of butyl acetate (10 mm Hg @ 68^{o}F) we can determine the evaporation rate. The vapor pressure must have been measured at the same temperature for this calculation to be valid. Table 7 illustrates the relationship between vapor pressure and evaporation rate for a few selected compounds.

Compound Name	Vapor Pressure @ 68^{O}F (20^{O}C)	Evaporation Rate	Boiling Point ^{O}F
Butyl acetate	10 mm Hg	1	260
Acetone	220 mm Hg	22	133
Arochlor 1254	0.0006 mm Hg	0.00006	689-734
Ethyl alcohol	43 mm Hg	4.3	172
Methyl ethyl ketone	70 mm Hg	7	175
Normal Pentane	426 mm Hg	42.6	97
Toluene	22 mm Hg	2.2	231

Table 7. Vapor Pressure, Evaporation Rate, and Boiling Point for a Few Selected Compounds

The greater the evaporation rate, the more volatile the liquid. In this example, ethyl ether and n-pentane would be considered extremely volatile while Arochlor 1254 (PCB) would be considered essentially non-volatile.

13.6 Boiling Point

The boiling point of a liquid is the temperature at which the vapor pressure of the liquid is equal to the atmospheric pressure at its surface. Since an increase in altitude produces a corresponding proportional decrease in pressure, substances at higher altitudes will boil at a lower temperature. Also, although water boils at 212°F at sea level, water vapor is produced at much lower temperatures. As water is heated, the rate of vapor formation increases. This same principle, which is referred to as *entropy*, applies to **all** liquids. Those with low boiling points at room temperature will evaporate or vaporize rapidly (are highly volatile) while those with high boiling points tend to vaporize very slowly.

Above the boiling point of a liquid, only vapors exist. Therefore, the only way to heat a liquid above its boiling point is to apply pressure in a closed container. To exceed the increased pressure, the boiling point of the liquid must be increased. As for example, in an automobile radiator. Similarly, a decrease in atmospheric pressure will result in a corresponding decrease in the boiling point.

13.7 Vapor Density

Vapor density is a measurement of the density of a gas or vapor compared to the density of the ambient atmosphere. Density is mass per unit volume. Air has a density of 1.29 g/L at standard temperature and pressure[1]. If the density of a vapor or gas is greater than that of the ambient air than the vapor or gas will tend to settle in the lowest available space. If the vapor density (**Vapd**) is close to the air density, the gas or vapor will tend to disperse in the atmosphere. When the vapor density is less than that of the surrounding air, the material will rise. Temperature and humidity also influence vapor density. Low ambient temperatures **increase** vapor density while high ambient temperatures **decrease** vapor density. This principle allows hot air balloons to rise—as the air is heated it becomes less dense and hence the air rises. Similarly, high humidity tends to **increase** vapor density, while low relative humidity will tend to **decrease** vapor density.

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[1] Standard temperature is 0°C and standard pressure is 1 atmosphere (760mm of mercury).

The OSHA Hazard Communication Standard and The Community Right-to-Know Law under SARA Title III have greatly increased the availability of hazard information primarily due to the accessibility of Material Safety Data Sheets (MSDS). However, a non-chemist may still find occasions where data is not readily available. Since knowledge of the vapor density is an important consideration, its calculation may prove useful. A basic familiarity with the Periodic Table will allow even the worst scientist to determine these values. The molecular weight of a compound is found by adding the atomic weight of each component, this value is then compared relative to air which weighs approximately 29 g/mol.

A **mole**, abbreviated mol, is a quantity of a substance, whether it be ions, atoms, or molecules equal to 6.023 x 10^{23}, or 602,300,000,000,000,000,000,000! This impossibly large number is known as Avagadro's Number and was first hypothesized by the Italian chemist, Amadeo Avagadro in the Eighteenth century. The atomic weights listed on the Periodic Table of the Elements were calculated by determining the weight of one mole of each substance. Thus, one mole of hydrogen atoms (H) weighs 1.008 grams, while one mole of hydrogen molecules (H_2) weighs 2.016 grams. The atomic weights are essential to the determination of vapor density.

The Density of Ambient Air

Nitrogen (N_2) = 14 g x 2 = [28 g/mol x 78%] = 21.84 g
Oxygen (O_2) = 16 g x 2 = [32 g/mol x 21%] = 6.72 g
Argon (Ar) = 40 g x 1 = [40 g/mol x 1%] = + 0.40 g
$\boxed{28.96\text{ g}}$

Rounding off we obtain 29 g/mol as the average molecular weight of air. Using the following simple formula, you can easily calculate any vapor density:

$$\boxed{\text{Vapor density} = \frac{M\,W}{29}}$$

The following example illustrates the calculation of the vapor density for carbon dioxide (CO_2).

Molecular weight of Carbon dioxide

1 atom of Carbon (12.0 g/mol) = 12.0 g
2 atoms of Oxygen (16.0 g/mol) = 32.0 g
44.0 g

Vapor density of CO_2

$$\frac{44.0}{29.0} = 1.52\text{; thus, carbon dioxide is 1.52 times heavier than air}$$

Vapor densities for a few selected compounds are listed in Table 8 below. See if you can calculate these yourself using the formula given for vapor density. Hint: The molecular formula for gasoline is C_8H_{18}. Use the Periodic Table to calculate the molecular weight.

Table 8. Vapor Densities of Selected Compounds

MATERIAL	VAPOR DENSITY
gasoline	3.0-4.0
toluene	3.14
chlorine	2.5
propane	1.6
ethylene	1.0
ammonia	0.6
methane	0.55
hydrogen	0.1

One further comment about vapor density. These densities were essentially calculated at room temperature. Increased temperatures drive the molecules further apart reducing the density of the gas or vapor while decreased temperatures increase the density of the gas or vapor.

Chapter 14. Compressed Gases

Of the three physical states of matter; solid, liquid, and gas—gases are among the most prevalent, and are perhaps the most hazardous. Six of the top ten chemicals produced annually in the United States are gases:

Nitrogen	#2
Ethylene	#3
Ammonia	#4
Oxygen	#5
Chlorine	#8
Propylene	#10

Two other gases, ethylene oxide and butadiene are also on the list of the top 50 chemicals. Often liquids are mistakenly referred to as gases because people confuse the terms gas and vapor. Two examples are methyl isocyanate and dichlorodiethylsulfide ("mustard gas"). Vapors are produced when liquids (or solids) evaporate. The physical state of a material at room temperature is the determining factor. Thus gases are gases at room temperature and vapors are liquids (or solids) at room temperature.

The Department of Transportation (DOT) 49 CFR 173.300 (a) and the Occupational Safety & Health Administration (OSHA) 29 CFR 1910.1200 use some arbitrary values to define compressed gases:

1. A gas or mixture of gases having, in a container, an absolute pressure exceeding 40 psi at 70 °F; or

2. A gas or mixture of gases having, in a container, an absolute pressure exceeding 104 psi at 130°F regardless of the pressure at 70 °F; or

3. A liquid having a vapor pressure exceeding 40 psi at 100 °F as determined by ASTM D-323-72.

14.1 Charles' Law and Boyle's Law

Note that temperature is integral to each of these definitions. The French scientist *Charles*, discovered that at a given pressure, the volume occupied by a gas is directly proportional to the temperature of the gas in °Kelvin.

This is known as **Charles' Law**. (Note: The Kelvin temperature scale is discussed below.)

Another important gas law was discovered by the English scientist Robert Boyle. Stated simply **Boyle's Law** says:

Double the pressure—half the volume

The inverse is also true. Half the pressure—double the volume. A temperature increase or a pressure decrease both result in a corresponding increase in the volume occupied by a gas. If there is no pressure relief mechanism available, as for instance, in a compressed gas cylinder, there is the distinct possibility of container failure, should the internal pressure of the cylinder exceed an established safety factor.

14.2 Temperature Measurements

Three Temperature Scales — A Comparison

	Farenheit	Celsius	Kelvin
water boils	212	100	373
	} 180	} 100	} 100
water freezes	32	0	273
absolute zero	-459	-273	0

Absolute zero is the theoretical temperature at which all molecular motion ceases. This is only measurable by extrapolating from higher temperatures since the probe needed to evaluate this temperature would not function if molecular motion ceased!

Conversions between degrees Farenheit and degrees Celsius are relatively simple if one understands the difference between the two scales: As noted above between the freezing point and the boiling point of water, there are 180 divisions on the Farenheit scale and only 100 on the Celsius scale. This ratio can be expressed as follows: $\boxed{180/100 = 1.8}$ Also on the Celsius scale water freezes at 0^{o} whereas on the Farenheit scale water freezes at 32^{o}. Taking these factors into consideration, we can establish two simple conversion equations:

For converting ^{o}F —> ^{o}C, use the formula $\boxed{^{o}F - 32 + 1.8 = {}^{o}C}$

For converting ^{o}C —> ^{o}F, use the formula $\boxed{^{o}C * 1.8 + 32 = {}^{o}F}$

Example problem 1:

What is the temperature in Celsius of a hot $102^{o}F$ July day ?

Solution: $(102^{o}F - 32) + 1.8 = 39^{o}C$

Example problem 2:

Ice milk can be conveniently prepared at $-10\ ^{o}C$. What is the Fahrenheit temperature ?

Solution: $(-10\ ^{o}C \times 1.8) + 32 = 14^{o}F =$ (a fairly cold temperature)

14.3 Some General Properties of Gases

1. Gases are compressible.
2. Gases will completely fill any container.
3. Different gases will form homogeneous mixtures (e.g. air).
4. Gases expand upon heating (principle of hot air balloons).
5. Gases do not settle in their container.

Chapter 15. Corrosive Materials

15.1 Introduction

As a hazard class, these may be the most common materials. Six of the top ten chemicals may inflict injury through corrosive action. As with flammable materials, corrosive chemicals come in all three physical states—solid, liquid, and gas. Corrosive solids and liquids must be placarded and labeled as **Corrosive Materials** per DOT regulations, while corrosive gases are normally labeled as **Non-flammable, Poison**, or both.

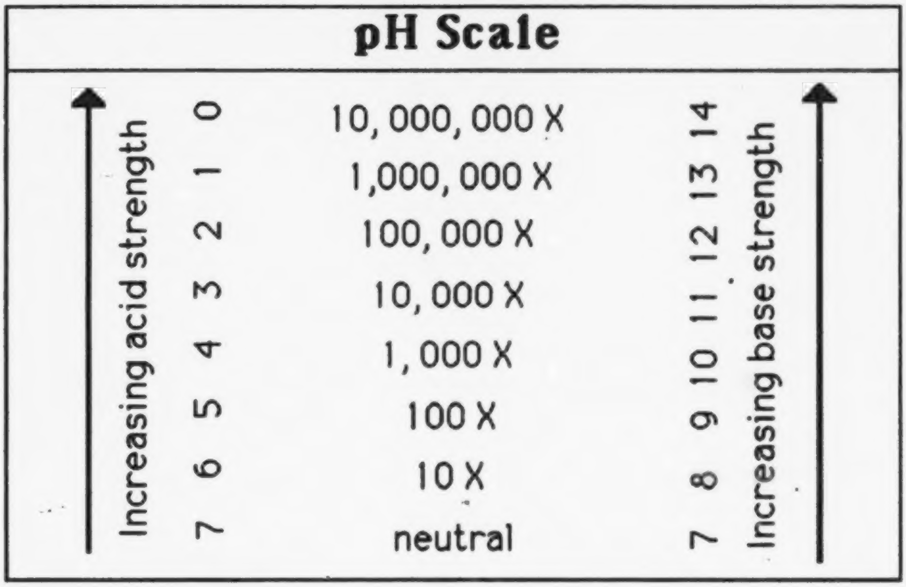
Corrosive materials are either acidic or caustic. The relative degree of corrosivity is determined based on the material's ability to dissociate or form ions in solution. Those that form the greatest number of hydrogen ions (H^+) are the strongest acids, while those that form the greatest number of hydroxide ions (OH^-) are the strongest bases. The measurement of the hydrogen ion concentration in solution is called the **pH**. (From the "power of hydrogen".)

15.2 The pH Scale

The pH scale is logarithmic. It is defined mathematically as the negative logarithm of the H^+ ion concentration (in moles/liter): $\boxed{pH = -\log [H^+]}$ As the H^+ ion concentration increases, the pH decreases. Strong acids have a low pH while strong bases have a high pH. The pH scale is ranges from 0 to 14 where each numerical increase on the pH scale represents a tenfold increase in acid or base concentration relative to pure water measured at 7.0. The following table illustrates this relationship.

Because this is a logarithmic scale, even massive dilution of concentrated acids may not reduce the pH to a "safe" level. In many cases, leaks or spills must be mitigated by neutralization. Neutralization is defined as: *"A chemical reaction in which water is formed by mutual destruction of the ions that characterize acids and bases. . ."* Neutralization does not mean attaining a pH of 7.0. When a strong acid reacts with a weak base, the pH will be below 7.0, and when a strong base reacts with a weak acid, the pH will be above 7.0.

Please note, the term "weak" when applied to acids and bases means that only a small portion of the substance in solution has formed ions. Weak is not a synonym for "dilute" which means that only a small amount of the substance is in solution. For example, vinegar, which contains 3-5% acetic acid (a "weak acid), has a pH of about 2.4-3.4 whereas a 4% hydrochloric acid solution has a pH of 0. This is because acetic acid (CH_3COOH) incompletely dissociates (ionizes) to form the simple hydrogen cation (H^+) and the complex acetate anion (CH_3COO^-). It is this degree of dissociation or ionization that determines the relative strength of an acid or base. You should realize that a dilute solution of a strong acid may have a higher pH (less acidic) than a concentrated solution of a weak acid. Table 9 lists pH values for some of the more common solutions.


pH Scale
Increasing acid strength
7 6 5 4 3 2 1 0
10,000,000 X
1,000,000 X
100,000 X
10,000 X
1,000 X
100 X
10 X
neutral
7 8 9 10 11 12 13 14
Increasing base strength

15.3 Acid Strength

Acid strength and acid concentration are not synonymous. Acid strength is determined relative to the degree of molecular ionization (separation) in water. For example, hydrochloric acid (HCl), will nearly completely separate in water to form H^+ ions and Cl^- ions; acetic acid ($HC_2H_3O_2$) by contrast, does not readily separate in water but rather retains its molecular structure. Acid concentration is dependent on the percentage of the acid in an aqueous solution. It is not an indication of corrosivity. Dilute strong acids may still be highly corrosive whereas concentrated weak acids may be relatively benign. NOTE: Water must be present to determine acid strength—a concentrated strong acid, e.g. 96% sulfuric acid is not as corrosive as 70% because the 4% water content in 96% acid limits the ionization. Acid strength is measured relative to pH. Very simply, the scale ranges from 0 — 14 with a neutral point of 7. Any value less than 7 is an increase in acidity; any value above 7 is a decrease in acidity. However a substance usually does not exhibit corrosive properties unless the pH is below about 3.0.

Table 9. The Approximate pH of Some Common Solutions

SOLUTION	pH
Hydrochloric acid (4%)	0
Gastric juices	1.6-1.8
Lemon juice	2.3
Vinegar	2.4-3.4
Soft drinks	2.0-4.0
Milk	6.3-6.6
Blood	7.35-7.45
Milk of magnesia	10.5
Sodium hydroxide (4%)	13.0

Acids or bases can produce immediate or acute effects in humans ranging from severe burns caused by skin contact to *pulmonary edema* (fluid in the lungs) caused by inhalation of concentrated vapors. For the purposes of environmental regulation, however, we will deal only with the statutory definition. EPA regulates only those acids with a pH less than or equal to 2.0, and bases with a pH greater than or equal to 12.5; or a liquid that has a corrosion rate on SAE 1020 steel of greater than 0.25 inch per year. A hazardous waste which exhibits the characteristic of corrosivity but is not otherwise listed in 40 CFR § 261, has the unique alphanumeric code **D002.**

15.4 Buffers

Buffers are another term with which you are probably familiar. A buffer is a solution that resists changes in pH when either an acid or base is added. Buffer solutions are critical to the human organism. For instance a pH imbalance in the blood can cause **acidosis** (low pH) which in extreme cases can cause shock, coma, and even death; or **alkalosis** (high pH) which in severe cases can lead to convulsions or death. A buffer solution contains two components in relatively large concentrations: a weak acid and a salt of that acid. For example, citric acid and sodium citrate form a buffer combination often found in commercial food products.

How does a buffer solution control pH? It contains a weak acid which reacts with bases and a weak base which reacts with acids to keep the pH at a desired level. When the buffer system is overloaded, as sometimes happens when excessive amounts of acidic food is consumed, a degradation of the stomach lining may occur resulting in the formation of an ulcer.

15.5 Baume´

This is an arbitrary scale of specific gravities originally devised by the French scientist, Antoine Baume´, and used in the graduation of hydrometers. This physical property is occasionally used as a reference to the concentration of an acid; as for instance, 66 Baume´, abbreviated 66 Be´. There are two formulas for calculating Baume´ depending on the specific gravity of the liquid. For liquids lighter than water (specific gravity less than 1.0), use formula 1; for liquids heavier than water (sg > 1.0), use formula 2:

$$\boxed{\text{Baume}' = \frac{140}{sg} - 130}$$

Formula 1

$$\boxed{\text{Baume}' = 150 - \frac{145}{sg}}$$

Formula 2

15.6 Corrosive Liquids

This is the most common type of corrosive material and consists of all the strong inorganic acids, as well as several organic acids. Most bases are solids but these are frequently made into solutions.

EXAMPLES:

Sulfuric acid	(98%)	sg = 1.84	71 Be´
Phosphoric acid	(85%)	sg = 1.69	64 Be´
Nitric acid	(70%)	sg = 1.41	47 Be´
Hydrochloric acid	(38%)	sg = 1.19	28 Be´
Sodium hydroxide (solutions)			

15.7 Hazards of Corrosive Liquids

1. Corrosive liquids may emit corrosive vapors.
2. Some vapors are more toxic than HCN (PEL: 11 mg/m^3)!!
   HF (PEL: 2.5 mg/m^3)
   NaOH (PEL: 2.0 mg/m^3)
   H_2SO_4 (PEL: 1.0 mg/m^3)

3. Caustic solutions are extremely destructive to the skin and eyes. A 2% NaOH solution causes irreparable damage to the eyes of rabbits within three minutes; a 50% NaOH solution causes irreparable damage within 15 seconds!

4. The H^+ ion produced by acids can attack metal by removing an electron to form the metal ion and hydrogen gas. It can also break apart or hydrolyze certain biologically important molecules such as proteins & enzymes thereby destroying skin, eye, and mucous membrane tissues.

5. A few of the stronger caustic solutions can react with certain metals, (e.g. aluminum, magnesium) to produce hydrogen gas.

15.8 Corrosive Solids

These include sodium hydroxide, also called caustic soda or lye and most of the bases. These materials tend to be somewhat deliquescent or hygroscopic (i.e. will readily absorb moisture).

EXAMPLES:	Sodium hydroxide	(caustic soda)
	Potassium hydroxide	(caustic potash)
	Calcium oxide	(unslaked lime)
	Calcium hydroxide	(slaked lime)
	Sodium carbonate	(soda ash)
	Sodium bicarbonate	(baking soda)
	Calcium carbonate	(limestone)

15.9 Hazards of Corrosive Solids

1. Inhalation of vapors or dusts may be harmful.
2. Corrosive effects on body are largely dependent on their solubility in skin, respiratory moisture, and contact duration.
3. Extreme evolution of heat when dissolving.
4. Lysis (breaking) of peptide bonds, severe degradation of tissue. Anesthetizing effect precludes awareness of damage.

15.10 Corrosive Gases

Corrosive gases are potentially the most injurious to life or health. These substances have been responsible for widescale evacuations. In 1979, a ruptured tank car of chlorine in Mississauga, Ontario caused the largest peacetime evacuation ever in North America when over 250,000 people were forced to leave their homes.

Since these substances are normally transported and stored under very high pressure, releases can easily result in exposure to large populations.

EXAMPLES:
Chlorine
Hydrogen Chloride
Hydrogen Fluoride
Anhydrous Ammonia
Phosphorus Pentoxide

15.11 Hazards of Corrosive Gases

1. Highly soluble gases are upper respiratory tract irritants.
2. Less soluble gases reach the alveoli easily, and nose or throat irritation may not occur. Delayed pulmonary edema can result.
3. Most gases are also skin contact hazards due to extreme solubility.
4. Liquified gases can cause frostbite and tissue necrosis.

5. Expansion ratios (liquid:vapor) may cause rapid depravation of oxygen. [NOTE: Vehicle may stall if driving through vapor cloud.]

6. Typical personal protective clothing may be inadequate if gas is liquified due to extreme cold.

Spotlight—Ammonia, A Corrosive We All Know

We have all had the shocking and pungent odor of ammonia hit our noses. It's one of those household smels that seems to say "its clean here". The name "ammonia" is very old and came from the *Ammonians* who worshipped the Egyptian god Amun. It is well known that this ancient civilization used ammonium chloride in their worship rites. It is said that these early people feared volcanoes because this is where ammonia smells arise from heating the ammonium chloride in cracks to give off ammonia and hydrochloric acid.

More molecules of ammonia are manufactured industrially each year than all other chemical compounds (because it is smaller than sulfuric acid molecules). Moreover, live itself relies on a process where atmospheric nitrogen (N_2) is changed to ammonia by only a few types of microbes. All the nitrogen in our body (DNA, RNA, and proteins) was once excreted by one of these microbes in a process called *nitrogen fixation.*

15.12 The Inorganic Halides

There are two other classes of corrosive chemicals—the **Halogens** and the **Inorganic Halides.** The first group is well known to most people and contains these four elements as diatomic molecules: Flourine (F); Chlorine (Cl); Bromine (Br); and Iodine (I). These were discussed earlier in Chapter 1. The Inorganic Halides are compounds which contain the ionic form of these same elements. Most are water reactive chlorides which produce hydrogen chloride gas (HCl) upon contact with atmospheric H_2O. The application of liquid water will produce tremendous volumes of HCl. Common industrial products of this type include aluminum trichloride ($AlCl_3$), and phosphorus pentachloride (PCl_5), which are solids; and phosphorus trichloride (PCl_3), phosphorus oxychloride ($POCl_3$), silicon tetrachloride ($SiCl_4$), and thionyl chloride, ($SOCl_2$), which are liquids. Chemically these substances are acids and can therefore be neutralized with weak bases.

15.13 Neutralization

In many cases, acid spills can be mitigated by neutralization. Neutralization is defined as: *"A chemical reaction in which water is formed* *by mutual destruction of the ions that characterize acids and bases"* Neutralization does not necessarily mean attaining a pH of 7.0. When a strong acid reacts with a weak base, the pH will be below 7.0, and when a strong base reacts with a weak acid, the pH will be above 7.0. If neutralization is considered as a course of action, certain factors should be evaluated including heat of reaction, expense, and disposal.

Once the decision is made, an appropriate type and quantity of neutralization agent must be obtained. A number of weak bases are readily available to neutralize acids. Four common materials are itemized in Table 10. **Note:** Strong bases such as sodium hydroxide should not be used to neutralize the spill of a strong acid.

CHEMICAL NAME	COMMON NAME	FORMULA
sodium carbonate	soda ash	Na_2CO_3
calcium hydroxide	"slaked lime"	$Ca(OH)_2$
sodium bicarbonate	baking soda	$NaHCO_3$
magnesium hydroxide	"milk of magnesia"	$Mg(OH)_2$

Table 10. Four bases commonly used for neutralizing acid spills.

The formula weight and specific gravity of the the four most common acids are listed to aid in determining neutralization. Specific gravity rather than density is used so that the weight of water (8.33 lbs/gal) can be used in all cases.

For the benefit of the Non-Chemists out there, I have omitted most of the formulae and calculations. What is provided is a simple method for determining the quantity of base needed to effectively neutralize a spill of one of four acids: sulfuric, hydrochloric, nitric, and phosphoric.

Acid	Wt. of Acid in 1 Gal	Specific Gravity
85% Phosphoric (H_3PO_4)	12.0 lbs	1.69
70% Nitric (HNO_3)	8.2 lbs	1.41
38% Hydrochloric (HCl)	3.8 lbs	1.19
96% Sulfuric (H_2SO_4)	14.7 lbs	1.84

Table 11. The four most common acids used in industrial applications.

As the physical state of most basic materials is solid, we need to know quantity, i.e. the weight of base needed to neutralize a spill. To compute this quantity, we must know the quantity, i.e. weight of acid that has spilled. Using one (1) gallon as a reference, we can readily determine the weight of a spilled acid. However, we must also know the specific gravity and the concentration of the acid. Four common acids and their concentrations are listed in Table 11. Consider the following example: One gallon of 96% sulfuric acid breaks on the floor of a research laboratory. An ample supply of soda ash is available to neutralize. How much is needed? First, compute the weight of the acid spilled according to the following formula:

Quantity of acid spilled (in gal) x specific gravity x 8.33 lbs/gal x percent acid = weight of acid in lbs

For our example:

1 gallon x 1.84 x 8.33 lbs/gallon x 0.96 = 14.7 lbs

To determine the amount of base necessary, you can use the conversion factors listed in Table 12 for the four neutralizing agents selected. All other factors being equal, consider cost when selecting a neutralizing agent. The lower the conversion factor, the lower the quantity of base needed to neutralize the spill. In most cases, magnesium hydroxide is the best choice.

Neutralizing agent	Sulfuric	Nitric	Hydrochloric	Phosphoric
sodium carbonate	1.082	0.841	1.452	1.622
calcium hydroxide	0.755	0.587	1.014	1.133
sodium bicarbonate	1.673	1.302	2.247	2.541
magnesium hydroxide	0.592	0.460	0.795	0.888

Table 12. Conversion factors (CF) for various acids and neutralizing media.

By multiplying the weight of acid spilled by the conversion factor for the selected base, one can determine the correct quantity necessary to neutralize the spill. For our example:

14.7 lbs acid spilled x **1.082** (CF for sodium carbonate) = **15.9** lbs of Na_2CO_3 needed

By estimating the quantity of acid spilled in gallons, we can develop a handy "cheat sheet" (see Table 13) for neutralizing acid spills: For a 10 gallon spill of sulfuric acid, 159 lbs of Na_2CO_3 are needed; for a 100 gallon spill, 1,590 lbs are needed; and for a 1,000 gallon spill, 15,900 lbs are needed. Computing the amount of neutralizing media for any size acid spill (figured in gallons) is easy. Simply multiply the number of gallons spilled by the appropriate conversion factor. If the concentration of the acid differs from those listed in Table 11, then the weight spilled should be recalculated using the new concentration and (ideally) a different specific gravity.

Amount of Sulfuric acid spilled	Quantity of Neutralizing Media needed
1 gallon	16 pounds
2 gallons	32 pounds
3 gallons	48 pounds
4 gallons	64 pounds
5 gallons	80 pounds
10 gallons	160 pounds
50 gallons	800 pounds
55 gallons	880 pounds
100 gallons	1,600 pounds

Table 13. "Cheat Sheet" for Neutralizing a Sulfuric Acid Spill Using Soda Ash

In actual practice some excess neutralizing agent should be obtained and the process monitored periodically by checking the pH of the reaction mixture. Neutralization is generally a somewhat exothermic reaction. Also remember the neutralization agent may have some hazard properties of its own. Adequate personal protective equipment including face shields, gloves, boots, and "rainsuits" and; in some cases, supplied air (SCBA or airline) must be worn to ensure the health and safety of personnel conducting the neutralization.

Chapter 16. Two Additional EPA Hazard Characteristics: Reactivity and Toxicity

There are two more characteristics of hazardous waste—one is the Toxicity Characteristic (TC) which will be explained later, the other is reactivity. The term reactive can be somewhat misleading in that the definition may vary slightly depending on the reference source used. To avoid any confusion, **reactivity** as defined here, is reprinted verbatim from **40 CFR § 261.23.**

16.1 Reactivity

(a) A solid waste exhibits the characteristic of reactivity if a representative sample of the waste has any of the following properties:

(1) It is normally unstable and readily undergoes violent change without detonating.

(2) It reacts violently with water.

(3) It forms potentially explosive mixtures with water.

(4) When mixed with water, it generates toxic gases, vapors or fumes in a quantity sufficient to present a danger to human health or the environment.

(5) It is a cyanide or sulfide bearing waste which, when exposed to pH conditions between 2 and 12.5, can generate toxic gases, vapors or fumes in a quantity sufficient to present a danger to human health or the environment.

(6) It is capable of detonation or explosive reaction if it is subjected to a strong initiating source or if heated under confinement.

(7) It is readily capable of detonation or explosive decomposition or reaction at standard temperature and pressure.

(8) It is a forbidden explosive as defined in 49 CFR 173.51, or a Class A explosive as defined in 49 CFR 173.53, or a Class B explosive as defined in 49 CFR 173.88.

(9) A solid waste that exhibits the characteristic of reactivity, but is not listed as a hazardous waste in Subpart D, has the EPA Hazardous Waste Number of D003.

16.2 Toxicity Characteristic

Prior to March of 1990, this was known as Extraction Procedure (EP) Toxicity. This referred to a procedure developed by the USEPA to replicate acidic conditions in a sanitary landfill caused by the decay of organic matter. However, with the passage of the Hazardous and Solid Waste Amendments Act of 1984 (HSWA), which includes a statutory mandate requiring synthetic liners, and the continually escalating costs associated with waste disposal in a hazardous waste landfill, co-disposal (the co-mingling of hazardous & non-hazardous waste) is no longer common practice.

Using the test method outlined in 40 CFR 261, Appendix II, a solid waste exhibits the toxicity characteristic (TC) if an extract from a representative sample of the waste contains any of the contaminants listed in Tables 14 or 15 at a concentration equal to or greater than the respective value given in the table which, in most cases, are 100 times the PDWS (public drinking water standard).

The TC testing protocol combines a much more viable, reproducible procedure with a bonafide quality control/quality assurance (QC/QA) program. As such the data obtained is more accurate and better representative of anticipated concentrations in a field setting.

A solid waste that exhibits the characteristic of toxicity has the unique alphanumeric hazardous waste code specified in Table 14 which includes the original fourteen (14) EP toxic contaminants or the code specified in Table 15 which represents the additional twenty-five (25) contaminants added to the list. These toxic contaminants are the so-called D-code wastes. e.g. Lead (D008) EPA has also deferred thirteen (13) other substances for which their fate and transport model did not accurately predict the anticipated results. These 13 substances will be added to this list once the necessary computations are met: Acrylonitrile, 1,1,1,2-tetrachloroethane, bis (2-chloroethyl) ether, 1,1,2,2-tetrachloroethane, carbon disulfide, 2,3,4,6-tetrachlorophenol, 1,2-dichlorobenzene, toluene, isobutyl alcohol, 1,1,1-trichloroethane, methylene chloride, 1,1,2-trichloroethane, phenol.

Table 14. Maximum Concentration of Contaminants for Toxicity Characteristic (original 14)

EPA waste number	Constituent	Maximum conc. (milligrams per liter)
D004	Arsenic	5.0
D005	Barium	100.0
D006	Cadmium	1.0
D007	Chromium	5.0
D008	Lead	5.0
D009	Mercury	0.2
D010	Selenium	1.0
D011	Silver	5.0
D012	**Endrin** (1,2,3,4,10-hexachloro-1,7 epoxy-1,4,4a,5,6,7,8,8a,-octahydro-1,4-endo,endo-5,8-dimethanonaphthalene	0.02
D013	**Lindane** (1,2,3,4,5,6-hexachlorocyclohexane, gamma isomer	0.4
D014	**Methoxychlor** (1,1,1-Trichloro-2,2-bis [p-methoxyphenyl] ethane)	10.0
D015	**Toxaphene** ($C_{10}H_{10}Cl_8$, Technical chlorinated camphene, 67-69 percent chlorine)	0.5
D016	**2,4-D**, (2,4-Dichlorophenoxyacetic acid)	10.0
D017	**2,4,5-TP Silvex** (2,4,5-Trichlorophenoxypropionic acid)	1.0

HSWA also mandated that Congress re-evaluate the EP test and make appropriate changes. In June, 1986, the new procedure was published in the Federal Register. After receiving comments from the regulated community, EPA revised the procedure slightly and added 25 organic compounds to the original list of 14 constituents. Thirteen other organic compounds were on the proposed list but due to difficulties with the test protocol, these were deferred. The additional 25 regulated compounds are listed below in Table 15.

Table 15. The 25 Toxicity Characteristic Organics

EPA HW[1] Number	Constituent	CAS[2] Number	Regulatory Level (mg/L)	Basis
D018	Benzene	7-43-2	0.5	MCL
D019	Carbon tetrachloride	56-3-5	0.5	MCL
D020	Chlordane	5-74-9	0.03	RSD
D021	Chlorobenzene	10-90-7	100.0	RFD
D022	Chloroform	6-66-3	6.0	RSD
D023	o-Cresol	9-48-7	200.0[4]	RFD
D024	m-Cresol	18-39-4	200.0[4]	RFD
D025	p-Cresol	16-44-5	200.0[4]	RFD
D026	Cresol		200.0[4]	RFD
D027	1,4-Dichlorobenzene	10646-7	7.5	MCL
D028	1,2-Dichloroethane	10706-2	0.5	MCL
D029	1,1-Dichloroethylene	75--4	0.7	MCL
D030	2,4-Dinitrotoluene	1214-2	0.13[3]	RSD
D031	Heptachlor (and its hydroxide)	76-8	0.008	RSD
D032	Hexachlorobenzene	11874-1	0.13[3]	RSD
D033	Hexachloro-1,3-butadiene	878-3	0.5	RSD
D034	Hexachloroethane	67-72-1	3.0	RSD
D035	Methyl ethyl ketone	78-93-3	200.0	RFD
D036	Nitrobenzene	98-95-3	2.0	RFD
D037	Pentachlorophenol	87-86-5	100.0	RFD
D038	Pyridine	110-86-1	5.0[3]	RFD
D039	Tetrachloroethylene	127-18-4	0.7	RSD
D040	Trichloroethylene	79-01-6	0.5	MCL
D041	2,4,5-Trichlorophenol	95-95-4	400.0	RFD
D042	2,4,6-Trichlorophenol	88-06-2	2.0	RSD
D043	Vinyl Chloride	75-01-4	0.2	MCL

1 Hazardous waste number

2 Chemical abstracts service number

3 Quantitation limit is greater than the calculated regulatory level. The quantitation limit therefore becomes the regulatory level.

4 If 0-m-, and p-cresol concentrations cannot be differentiated, the total cresol (D026) concentration is used. The regulatory level for total cresol is 200 mg/L.

Chapter 17. Toxicological Properties

17.1 Exposure

"Exposure" or "exposed" as defined by OSHA under Hazard Communication (29 CFR 1910.1200) means: ". . .*that an employee is subjected to a hazardous chemical in the course of employment through any route of entry (inhalation, ingestion, skin contact or absorption, etc.) and includes potential (e.g. accidental or possible) exposure.*" The terminology "subjected to" is too inspecific for empirical evaluation. However, OSHA also has established specific exposure limits (airborne concentrations) for 600 industrial chemicals. These are referred to as **Permissible Exposure Limits** or **PELs** and are usually expressed in parts per million (ppm).

17.2 Threshold Limit Values

Soon after the passage of the Occupational Safety and Health Act of 1970, The Occupational Safety and Health Administration (OSHA), pursuant to the rulemaking authority granted under section 6(a) of the Act, adopted the exposure levels set by the American Conference of Governmental Industrial Hygienists (ACGIH) in 1968 for some 400 chemicals. ACGIH used the term **Threshold Limit Value** or **TLV©** for these exposure limits and based "exposure" on an 8-hour Time Weighted Average (TWA). This concept stipulated that the average individual could be exposed at or below the TLV-TWA for 8 hours per day, 5 days per week with no deleterious effects. OSHA was unable to adopt the same terminology due to the TLV copyright and thus introduced the term "Permissible Exposure Limit". The exposure limits, however, remained identical to the 1968 TLV figures.

ACGIH amends their TLVs annually as dictated by an increased awareness of the toxicological properties of certain industrial chemicals. OSHA, unfortunately, did not provide a mechanism for timely changes to the PELs. In December 1991, OSHA attempted to correct the problem. Table Z-1-A of 29 CFR Part 1910 was been amended to include 164 new substances, more protective exposure limits were established for 212 substances, and 224 PELs remain unchanged. A detailed breakdown is depicted graphically in Figure 3.

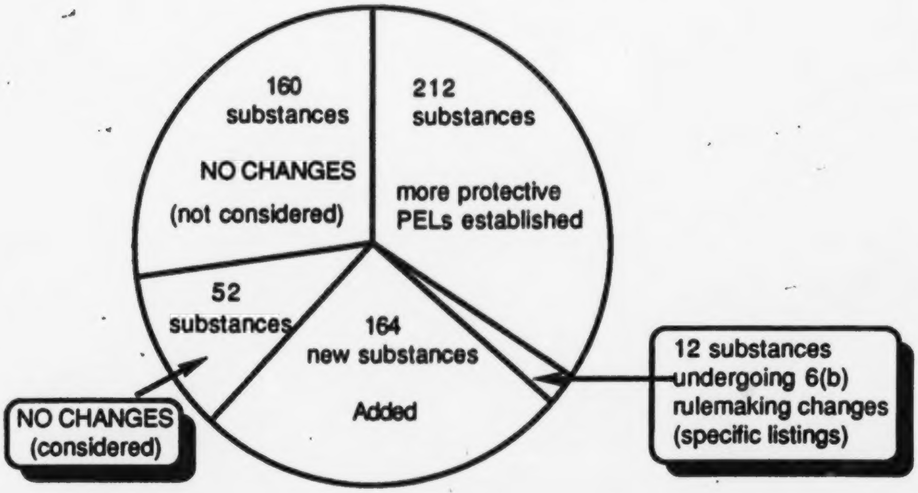


Figure 3. The New OSHA PELs

ACGIH lists three other exposure limits: **TLV-C**; **TLV-STEL**; and **TLV-SKIN**. These are defined herein.

TLV-C (TLV-Ceiling) This concentration should not be exceeded at any time during the work day, even instantaneously.

TLV-STEL (TLV-Short Term Exposure Limit) The maximal concentration to which workers can be exposed for up to 15 minutes without suffering from any of the following symptoms:

i) irritation;
ii) chronic or irreversible tissue change;
iii) narcosis of sufficient degree to increase accident proneness, impair self-rescue, or materially reduce work efficiency.

No more than four excursions to the STEL are permitted daily and these must be separated by a period of at least 60 minutes. (NOTE: OSHA regulations prohibit exceeding the STEL more than once per day).

TLV-SKIN Nearly one-fourth of the substances in the TLV list are followed by the designation "SKIN". This notation is usually indicative of high skin, eye, or mucous membrane absorption rates. This is an attentiongetting term, designed to help prevent skin contact so the TLV-TWA is not invalidated.

17.3 I.D.L.H. Level

There is one additional listed exposure level—**IDLH** which is an acronym for **Immediately Dangerous to Life or Health.** NIOSH defines IDLH as *". . . a maximum concentration from which, in the event of respirator failure, one could escape within 30 minutes without experiencing any escape-impairing or irreversible health effects."*

OSHA incorporated the IDLH term in their Worker Protection Standard for Hazardous Waste Operations and Emergency Response [29 CFR 1910.120] in December, 1986. However OSHA excised the 30-minute escape period. IDLH as defined by OSHA means: *". . . a corrosive, toxic, or asphyxiant atmosphere which causes serious irreversible health effects or death."*

EXAMPLE: Benzene

IDLH	2000 ppm	NIOSH
TLV-TWA	10 ppm (carcinogen)	ACGIH
PEL-TWA	1 ppm (carcinogen)	OSHA
PEL-STEL	5 ppm	OSHA

Acute symptoms may occur at 7500 ppm within 30-60 minutes. Exposure is generally fatal within 5-10 minutes at 20,000 ppm

CHEMICAL	PEL	TLV	REL
Toluene Diisocyanate	0.02 ppm	0.005 ppm	0.005 ppm
Trichloroethylene *Ca	100 ppm	50 ppm	25 ppm
Sulfur Dioxide	5 ppm	2 ppm	0.5 ppm
Formaldehyde *Ca	1 ppm	1 ppm	0.016 ppm
Carbon Dioxide	5,000 ppm	5,000 ppm	10,000 ppm

Table 11. A comparison of some exposure values

But what actually constitutes an exposure? Understanding the relationship between percent and parts per million (ppm) will allow us to make an intelligent evaluation. Consider the following:

100% = 1,000,000 parts per million
50% = 500,000 parts per million
10% = 100,000 parts per million
1% = 10,000 parts per million

An atmosphere is tested for oxygen content and found to be 19.5%. OSHA accepts this as adequate level for entry into a confined space (ANSI Z88.2-1969). Ambient air, however, contains 20.9% oxygen, a difference of 1.4%. [This value is the equivalent of 14,000 parts per million.] NOTE: This takes into account only the displacement of oxygen. No gas or vapor will preferentially displace oxygen in air. Any gas or vapor present will displace AIR, that is oxygen **and** nitrogen. And air is comprised of 78% nitrogen—a value nearly 4 times greater than the oxygen content. If our hypothetical gas or vapor has displaced 1.4% oxygen, it must have then displaced 5.6% nitrogen (4 x 1.4%). The total volume of air displaced is 7.0% (1.4% + 5.6%) or 70,000 parts per million! If the contaminant is a simple asphyxiant such as methane it may be no problem. However, even a carbon dioxide atmosphere (PEL = 5,000 ppm) would exceed the acceptable exposure level by 65,000 ppm (6.5%)!

Workers are well-advised to head the standard operating procedures for confined spaces used by the U.S. Coast Guard. If the oxygen content is lower than 20.8% without certain knowledge of the contaminant, entry to confined spaces is only attempted in supplied air.

Exposure levels are sometimes expressed as milligrams per cubic meter (mg/m^3). These units are normally used to describe airborne concentrations of particulate material (e.g. dusts, mists) whereas ppm is normally used for airborne concentrations of gaseous contaminants. For comparison purposes, or otherwise, it may be necessary to convert from ppm to mg/m^3. The calculation is a simple one:

$$\boxed{mg/m^3 = ppm * \frac{MW}{24.45}}$$

where: mg/m^3 = milligrams per cubic meter
ppm = parts per million
MW = molecular weight in grams
24.45 = liters occupied by 1 mole of gas at 25°C

Example: The PEL for hydrogen cyanide (HCN) is 10 ppm. The molecular weight of HCN is 27 g. Its exposure level in mg/m^3 = 10 ppm $* \frac{27}{24.45} = 11$ **The PEL equals either 10 ppm or 11 mg/m^3**

17.4 Toxicity Considerations

The toxicity of a substance is determined based on one of the following properties:

1. Target organ effects
2. Physiologic action
3. Intended use
4. Source
5. Biochemistry
6. Physical state

The quantity or dose, the exposure duration, and the route of entry influence these effects. Toxicologists refer to this as the **Dose-Response Relationship.** If either the dose, or the exposure time is kept low enough, there will be no response. Remember though, toxicity is an inexact science, and is based on statistical averages.

> "Every substance is a poison. There is no substance which is not a poison. The right dose differentiates a poison from a remedy."
> Paracelsus (16th century)

17.5 Toxic Responses

There are many symptoms which may result from overexposure to chemicals. Per 29 CFR 1910.1200, **Chemical Hazard Communication,** employees working with hazardous chemicals must be made aware of symptoms which could occur if they are "exposed". Some of these are listed below:

RESPONSE:	EXAMPLES:
1. Biochemical	Cyanide, Carbon Monoxide
2. Behavioral	Mercury, Lead
3. Physiologic	Ammonia, Chlorine
4. Pathologic	Vinyl Chloride (liver)
5. Reproductive	X-rays
6. Carcinogenic	Benzene, Asbestos
7. Mutagenic	Radiation
8. Teratogenic	Thalidamide, Dinoseb

Besides corrosive and irritant atmospheres, there are two primary groups of toxic chemicals which produce debilitating effects in exposed individuals. These are **systemic poisons** and **asphyxiants**. We can subdivide these groups as shown:

SYSTEMIC POISONS

HEPATOTOXIC AGENTS

Carbon Tetrachloride
Vinyl chloride

- cause liver disorders

NEPHROTOXIC AGENTS

halogenated hydrocarbons

- cause kidney disorders

HEMATOPOIETIC TOXINS

aliphatic alcohols, e.g. MeOH
Aniline
Toluidine
Nitrobenzene
Benzene
Phenols

- cause blood disorders

NEUROTOXIC AGENTS

Methanol (methyl alcohol)
"heavy" metals, e.g. lead
organophosphorus pesticides

- affect the brain & CNS

ANESTHETICS/NARCOTICS

acetylene hydrocarbons
olefins (alkenes)
Ethyl Ether, Isopropyl Ether
aliphatic ketones, e.g. MEK
esters, e.g. Ethyl Acetate

- may cause dizziness, drowsiness, headache, etc.

ASPHYXIANTS

SIMPLE ASPHYXIANTS	CHEMICAL ASPHYXIANTS
Helium	Methyl Aniline
Argon	Cyanogen
Hydrogen	Hydrogen Cyanide
Carbon Dioxide	Carbon Monoxide
Nitrogen	Aniline
aliphatic hydrocarbons, e.g. Methane	
• displace oxygen causing suffocation	• chemically react to cause oxygen depravation

Combined effects may also occur. There are four types of combined effects. The effect may be either beneficial or otherwise:

Combined Effect	**Equation**	**Result**
Additive effect	2 + 2 = 4	more severe
Synergistic effect	2 + 2 = 5+	very severe
Antagonistic effect	2 + 2 = 0	less severe
Potentiation effect	2 + 0 = 3	more severe

Spotlight—Health Hazards as Hazardous Materials

"*Health Hazard* means a chemical, mixture of chemicals, or a pathogen for which there is statistically significant evidence based on at least one study conducted in accordance with established scientific principles that acute or chronic health effects may occur in exposed employees. The term 'health hazard' includes chemicals which are carcinogens, toxic or highly toxic agents, reproductive toxins, irritants, corrosives, sensitizers, hepatotoxins, nephrotoxins, neurotoxins, agents which act on the hematopoeitic system, and agents which damage the lungs, skin, eyes, or mucous membranes. . . "

This definition originated in OSHA's Hazard Communication Standard [29 CFR 1910.1200] in November, 1983 but was revised by OSHA in 1986 with the introduction of "Worker Protection Standard" [29 CFR 1910.120].

The Occupational Safety and Health Administration (OSHA) has been actively involved in regulation hazardous materials since the passage of the Occupational Safety & Health Act in 1970. As introduced, this statute was substance-specific. OSHA's role in the HazMat arena intensified in November 1983 when the Hazard Communication rule was introduced [48 FR 53280]. This standard required all manufacturers in Standard Industrial Classifications (SIC) codes 20-39, i.e. chemical producers, to prepare and make available to employees Material Safety Data Sheets (MSDS) for all hazardous chemicals in their workplace, to mark all containers with appropriate hazard warning labels, to have a written program, and to train all employees who may be exposed to a hazardous chemical. In August of 1987, OSHA expanded this standard to apply to all SIC codes, 01-89. [see 52 FR 31877]. A hazardous chemical by definition [29 CFR 1910.1200] is a chemical which is a physical hazard or a health hazard. "Physical hazard" refers to a chemical which is flammable, combustible, explosive, a compressed gas, an organic peroxide, an oxidizer, pyrophoric (ignites on contact with air), unstable, or water-reactive. These properties are intrinsic to the materials themselves whereas health hazards deal with the probable effects of chemicals on the human organism.

OSHA redefined the term "health hazard" in December, 1986. In October, then President Reagan had signed the Superfund Amendments & Reauthorization Act (SARA). This legislation was conceived after the tragedy in Bhopal, India and was primarily directed at protecting local communities in the United States from a similar disaster. Hence Title III. It is a lesser known component of that law, Title I, that involves OSHA. This title mandated the creation of a new worker protection standard for hazardous waste site operations and emergency response [51 FR 45654]. Title I requires 24 hours of training for all employees engaged in emergency response outside their normal work areas. Part of this training must include "recognition of safety & health hazards". A safety hazard is easily recognizable. It may involve inadequate lighting, ungrounded electrical outlets, limited means of egress, etc. A health hazard is bit more mysterious. According to OSHA, it is: 1) a chemical; 2) a mixture of chemicals; or 3) a pathogen [a causative agent of disease] for which there is statistically significant evidence based on at least one study. . . that acute (i.e. immediate) or chronic (i.e. long-term) effects *may* occur in exposed employees. Included are: carcinogens, toxic or highly toxic agents, reproductive toxins, irritants, corrosives, sensitizers, hepatotoxins, etc.

These substances all induce or may induce some type of chemical change in humans. The reason for such broad coverage of all chemicals is the dearth of knowledge governing toxicity. Of the more than 50,000 chemicals in common commercial use, only 284 have been tested by the government in the past ten years. Of those, only about half (144) have been shown to cause cancer in animals. In addition, there are a few chemicals which are proven human carcinogens such as benzene and vinyl chloride. In the absence of sufficient data on the adverse effects of chemicals on the human organism, and as only 53 of the 144 animal carcinogens are regulated by OSHA, the health hazard definition was developed to protect workers against all known or suspected toxic effects.

The specific impact of these health hazards is related to the chemical change they produce. All health hazards involve some type of chemical change which causes an aberration in the body: **carcinogens** cause the production of harmful tumors; **toxic or highly toxic agents** are determined relative to a minute oral or dermal lethal dose which kills 50% of the test animals [i.e. the LD_{50}]; **reproductive toxins** are either mutagens which cause damage to the chromosomes, or teratogens which damage the developing fetus; **irritants** are not corrosives which cause a reversible inflammatory effect; **corrosives** cause visible destruction of tissue at the point of contact; **sensitizers** cause a substantial number of exposed people to develop an allergic reaction after repeated exposure; **hepatotoxins** produce damage to the liver; **nephrotoxins** produce damage to the kidney; **neurotoxins** produce their primary effect on the nervous system; **agents which act on the blood or the hematopoietic system**, such as carbon monoxide or cyanide, interfere with the body's ability to use oxygen; **agents which damage the lung** cause irritation or damage to pulmonary tissue; **agents which damage the skin** have an adverse effect on dermal tissue; and **agents that damage the eye** are those that affect the eye itself or visual capacity.

This list describes some of the symptoms which may result from overexposure to certain chemicals. However, overexposure is a relative term since a very small dose may affect one individual while another individual may exhibit no effect at all. Take the case of butyl acrylate. A case in Kentucky involved exposure of several persons to this chemical during cleanup of a spill in 1983. A few persons complained of chemical burns to the mouth, nose, eyes, and upper respiratory tract but one individual was more severely affected than the others and may now be dying as a result of his exposure. OSHA does not list a permissible exposure level (PEL) for butyl acrylate but there is an established threshold limit value (TLV) of 10 ppm for this chemical. That TLV is equal to the PEL for hydrogen cyanide—an extremely hazardous material. Because federal regulations did not exist regarding exposure to this chemical, individuals were improperly protected. The new OSHA standards correct this deficiency with the all-encompassing "health hazard" definition.

This definition, while seemingly burdensome, represents an intelligent attempt to protect the health of the employees working with chemicals. Chemical Abstract Services (CAS) currently lists over 12 million chemicals in their database. Our toxicological knowledge of these is infinitesimal by comparison. Hazardous materials exist for our benefit—let us ensure the benefits outweigh the hazards, not vice-versa.

DEPARTMENT OF TRANSPORTATION DEFINITIONS
CLASSES OF HAZARDOUS MATERIALS

CLASS 1 - EXPLOSIVES see 49 CFR 173.50

Division 1.1	Explosives which have a mass explosion hazard.
Division 1.2	Consists of explosives which have a severe projection hazard
Division 1.3	Consists of explosives that have a fire hazard and either a minor blast hazard or a minor projection hazard or both
Division 1.4	Explosives which present a minor blast hazard
Division 1.5	Consists of very insensitive (stable) materials
Division 1.6	Consists of extremely insensitive detonating substances

CLASS 2 - COMPRESSED GASES

Division 2.1	**Flammable Gas.** A material that is a gas at 20°C or less, and at 101.3kPa (14.7 psi) of pressure is either (1) ignitable when in a mixture of 13% or less by volume in air, or (2) has a flammable range in air of at least 12 percent regardless of the lower limit. **49 CFR 173.115 (a)**
Division 2.2	**Non-Flammable Gas.** A non-flammable, non-poisonous compressed gas which exerts as absolute pressure of 280 kPa (41 psi) at 20°C in the packaging. This division also includes materials defined as: non-liquefied compressed gas; liquefied compressed gas; compressed gas in solution and cryogenic liquids. **49 CFR 173.115 (b)**
Division 2.3	**Poisonous Gas.** A material which is a gas at 20°C or less, has a pressure of 101.3 kPa (14.7 psi) and is either (1) known to be so toxic to humans as to pose a hazard to health during transportation, or (2) when tested on laboratory animals, has an LC_{50} value of not more than 5000 ppm. Gases in this division are further split into Hazard Zones A through D bases on inhalation toxicity values. **49 CFR 173.115 (c)**

CLASS 3 - FLAMMABLE LIQUIDS

Flammable liquid. Any liquid with either (1) an initial boiling point less than 35°C (95°F) regardless of the flash point; of (2) any liquid having a closed cup flash point below 60.5°C (141°F). The boiling point and flash point determines to which of the three Packing Groups I, II, or III the material is assigned. **49 CFR 173.120 (a)**

Combustible liquid. Any liquid not meeting another hazard class with a flash point above 60.5°C (141°F) and below 93°C (200°F). **49 CFR 173.120 (b)**

CLASS 4 - FLAMMABLE SOLIDS

Division 4.1	**Flammable Solids.** Includes (a) Wetted explosives; (b) Self-reactive materials that are liable to undergo a strongly exothermal decomposition caused by excessively high transport temperatures or by contamination; and (c) Readily combustible solids that (1) may cause a fire through friction, (2) show a burning rate faster than 2.2 mm per second, (3) metal powders than can be ignited and react over the entire length of a sample in 10 minutes or less. **49 CFR 173.124 (a)**
Division 4.2	**Spontaneously combustible material.** Either (a) A pyrophoric material that can ignite within five minutes after contact with air; (b) A self-heating material that spontaneously ignites; (c) A tested sample that exceeds 200°C during a 24-hour test period. **49 CFR 173.125 (b)**
Division 4.3	**Dangerous When Wet.** A material that is liable, after coming in contact with water, to become spontaneously flammable or to give off flammable or toxic gas at a rate greater thanone liter per kilogram of material per hour. **49 CFR 173.125 (c)**

CLASS 5 - OXIDIZERS AND ORGANIC PEROXIDES

Division 5.1	**Oxidizer.** A material which may, generally by yielding oxygen, cause or enhance combustion of other materials. These materials may be either solids or liquids.
Division 5.2	**Organic Peroxide.** Any organic compound containing oxygen in the bivalent -O–O- structure, and which may be considered a derivative of hydrogen peroxide where one or more of the hydrogen atoms have been replaced by organic radicals. These materials are further separated into Generic Types A through G. **49 CFR 173.128 (a) (b)**

CLASS 6 - POISONOUS AND INFECTIOUS SUBSTANCES

Division 6.1	**Poisonous Material.** A material, other than a gas, which is known to be toxic to health during transportation. In the absence of adequate data on human toxicity, animal toxicity may be used to measure acute oral, dermal, and inhalation toxicity levels. **49 CFR 173.132, 173.133**
Division 6.2	**Infectious Substances.** a viable microorganisms or a toxin which causes or may cause disease in humans or in animals. Also included in this class are **Diagnostic and Biological specimens. 49 CFR 173.134**

CLASS 7 - RADIOACTIVE MATERIAL

Materials that emit radiation at an activity greater than 0.002 microcuries per gram. This may include uranium or thorium ores, unirradiated natural or depleted uranium, or unirradiated natural thorium. **49 CFR 173.403**

CLASS 8 - CORROSIVE MATERIAL

A liquid or solid that causes visible destruction or irreversible alterations to human skin, or a liquid that severely corrodes steel or aluminum surfaces. A material is considered to be destructive or to cause irreversible alterations in human skin tissue if, when tested on the intact skin of the albino rabbit, the structure of the tissues at the site of contact is destroyed or changed irreversibly after an exposure period of four hours or less. (New test methods using artificial biobarriers are also acceptable) **49 CFR 173.136 (a)**

CLASS 9 - MISCELLANEOUS HAZARDOUS MATERIALS

Any material which presents a hazard during transport, but which is not included in any other hazard class. **Class 9** includes: (a) Any material whcih has an anesthetic, noxious or other similar property which could cause extreme annoyance or discomfort to a flight crew member so as to prevent the correct performance of asssigned duties, e.g. **Formaldehyde solution** or **Carbon dioxide, solid**; and (2) Any material that is not included in any other hazard class, but is subject to DOT regulations. This category would include any material described as either **Environmentally Hazardous Substance, liquid or solid, n.o.s.** or **Hazardous Waste, liquid or solid, n.o.s.**

MARINE POLLUTANTS

A marine pollutant is a material that is listed in Appendix B to 172.101 and when in a solution or mixture of one or more marine pollutants, is packaged in a concentration which equals or exceeds: (1) Ten percent by weight of the solution or mixture; or (2) One percent by weight of the solution or mixture for materials that are identified as severe marine pollutants (PP) in Appendix B